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Development of In-Situ Techniques for the Detection and Measurement of Corrosion of Copper Concentric Neutrals in Underground Environments

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Chemical Stability and Corrosion Division
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National Bureau of Standards
Washington, D.C. 20234

June 1978

Annual Report

Prepared for
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Executive Summary

In the second year of a three year project aimed at developing techniques and instrumentation for detecting and measuring corrosion on copper concentric neutral (CCN) wires, the following points were accomplished:

- 1) Current-potential and ac impedance measurements on a number of specimens have been performed in the laboratory under different environmental conditions, and the data analyzed.
- 2) The development of equipment and techniques for the employment of electrochemical noise as a diagnostic tool has continued. A special potentiostat has been built and tested.
- 3) Potential and polarization measurements on buried cables in the field have been carried out. A number of sources of interference have been found, and techniques for minimizing their effect on the measurements have been developed.
- 4) Examination of portions of the buried cables, and modification of the soil in order to accelerate corrosion have been carried out.

In the coming year it is planned to correlate polarization measurements of corrosion with visual inspection, test various laboratory developed techniques in the field, carry out measurements in larger cable systems and on an actual operating cable.

1. Introduction

This is the second annual report of a three year project whose objective is to develop techniques for detecting and measuring corrosion on copper concentric neutral (CCN) wires buried in the soil.

During the first year, efforts in the laboratory were directed at finding the conditions that produce rapid localized corrosion as observed in the field. This was accomplished as reported in our annual technical report of January 1977. Also, during the first year specimens were prepared and buried at the outdoor NBS site, and preliminary measurements were made on these specimens. In the year covered by this report, 1977, our immediate objective was to bring the findings in the laboratory to bear on the measurements at the outdoor test site.

The laboratory work consisted in testing polarization and impedance measurements on CCN wires in electrolytic cells under various conditions, and in developing and testing instrumentation for the measurement of electrochemical noise, a technique that shows promise of eventual application in the field.

A major part of the work in the past year has been directed to the development of field measurement techniques on actual CCN cables buried underground, both in the presence and in the absence of a superimposed ac signal. Some experiments on the effect of modifying the composition of the soil on electrochemical measurements has also been carried out.

2. Laboratory Studies

2.1 Polarization measurements

In order to provide useful data for assessing the significance of polarization measurements on buried cables, tinned CCN wire

electrodes immersed in neutral Na_2SO_4 solution gelled with agar, with and without the addition of NaCl , have been tested, taking current-potential readings at long time intervals. The results have been analyzed using the curve-fitting method developed by Mansfeld (1). For this purpose a program to be used on a desk calculator was developed. The parameters derived from the analysis of the polarization curves are summarized in Tables I and II. In the tables the open circuit potential (O.C.P.) versus the normal hydrogen electrode (NHE) as well as the corrosion current density I_{corr} are reported. The constant B , whose meaning is explained in equation (1), and the anodic and cathodic Tafel slopes b_a and b_c are also given, as they are obtained from the curve-fitting program. The quality of the fit is also indicated. Where no fit was possible, the corrosion current was estimated with the linear polarization method.

The fitting of the experimental values to the fundamental equation of electrode kinetics was found to depend quite strongly on the value chosen for the open circuit potential, which particularly affected the value of the Tafel slope constants. For these reasons, some of the values listed in the tables are considered of doubtful reliability.

In spite of the scatter caused by the difficulty in choosing the optimum fitting conditions, a number of general conclusions can be drawn:

a) Corrosion currents tend to decrease with time, indicating that corrosion products have some protective value at least if no removal is possible as it is in agar gelled solutions.

b) The presence of chlorides tends to increase the corrosion current.

c) The value of the constant B, necessary for the evaluation of the corrosion current I_{corr} from simple linear polarization measurements according to the equation

$$i_{\text{corr}} = \frac{\Delta i}{\Delta E} \cdot \frac{1}{B} = \frac{1}{R_p B} \quad (1)$$

lies between 20 and 30 mV.

d) Concerning the cathodic Tafel slope b_c , it was expected to find a value of infinity in every case, since the cathodic process is supposed to be the diffusion controlled reduction of oxygen. Very large values of b_c were actually found in many cases: however, values between 100 and 200 were also frequently calculated by the curve-fitting program. A tentative explanation is that some of the oxidation products of the CCN wire (either copper or tinning alloy) were being reduced during cathodic polarization. This would be in agreement with the results of the potentiodynamic scans, described in the previous annual report, where cathodic peaks were found on tinned wire and on pure copper in chloride containing solutions. Reduction of corrosion products should be made more likely in these experiments where, as in the soil, even soluble corrosion products cannot be removed by convection. These results, therefore, can be significant for the interpretation of the field measurements.

e) No easily detectable differences were found between specimens exposed to an ac signal and those not so treated. Since visual observation of the specimens has not been performed yet, it is not known whether pitting has occurred at a different rate on the two

types of specimens. However, it should be stressed that the polarization measurements were always performed while the ac signal was disconnected. The failure to detect a significant difference in polarization resistance between specimens with and without ac once this signal is removed, indicates the need to carry out these measurements when the ac signal is being applied.

2.2 Impedance measurements

Impedance measurements, which have been extensively used in electrode kinetics research (2), are being applied to corrosion studies (3). These measurements are very attractive, because if the electrode system under investigation can be considered as consisting of a resistor R_S in series with a parallel combination of a resistor R_E and a capacitor C_E , a plot of the imaginary impedance Z'' versus the real impedance Z' will give R_S as the limit of Z' when the frequency approaches infinity and $(R_E - R_S)$ as the limit of Z' when the frequency approaches zero. The physical interpretation of R_S is the resistance in the electrolyte that causes the ohmic drop error, and R_E is the electrode or polarization resistance, in the absence of complicating kinetic factors at the electrode. Additional information can be obtained by a careful analysis of the curves, but obtaining polarization resistance and ohmic drop would be sufficient for estimating corrosion rates.

During this year impedance measurements have been made on a number of cells where the electrode was a piece of tinned CCN wire in solutions gelled with agar and under various environmental conditions. The results obtained are summarized in Tables III, IV, V and VI, and some of them are presented in graphic form in fig. 1 and 2.

Examination of the results shows that the high frequency limit of Z' is at the most a few ohms, indicating a negligible R_s and therefore a very small ohmic drop error. On the low frequency side the readings were limited to 5 Hz by our equipment, and all the curves show that this frequency is still too high to allow a measurement of the reaction resistance. Differences due to the experimental conditions can be derived from the tabulated values, but a large scatter in the data taken at various times since the tests began obscures the significance of other factors and makes interpretation difficult. The impedance is larger (at the same frequency) in solutions without chlorides and in the presence of oxygen. This might indicate that a more protective film forms in the absence of chlorides, but since the frequency range is limited, it is impossible to draw reliable estimates of the reaction resistance. The impedance seems to be larger for samples to which no a.c. signal has been applied, and perhaps there is a trend to larger values with time. The scatter of the results, however, makes these conclusions highly speculative.

A peculiar shape in the $Z'-Z''$ curves for specimens in N_2 had been observed and mentioned in a previous quarterly report. This was a semicircle at the high frequency end of the plot, suggesting a complex electrode reaction. Curves showing this feature are shown in fig. 2. Unfortunately subsequent careful measurements were never able to show this feature again. The new curves obtained are also shown in fig. 2.

We have also tried to extend the frequency range of the impedance measurements more than two orders of magnitude. These measurements are very time-consuming and therefore only a few attempts have been made. Fig. 3 and 4 show results for a wire in nitrogen and one in oxygen.

Both figures show that it would be necessary to extend the low frequency well beyond 10 MHz, which is our limit at the present time. The results are therefore inconclusive: in the case of Na_2SO_4 in N_2 (fig. 3) Z'' is still rising at 0.02 Hz. Although the plot would not be inconsistent with a reaction resistance of the order of $150\text{k}\Omega\cdot\text{cm}^2$, and therefore with a corrosion current of a few tenths of a $\mu\text{A}/\text{cm}^2$, as obtained from polarization measurements on the same cell (see table I), it could be argued that the impedance is due to diffusion processes. Fig. 4, obtained in an oxygen atmosphere is also inconclusive. If it is possible that the plot shows the existence of two electrode reactions with two time constants, but since no maximum in Z'' could be observed no firm conclusions can be drawn.

Impedance measurements therefore do not show much promise to become a useful diagnostic tool for the purposes of this project for two reasons: a) a large scatter in the results obscures their significance, and this is likely to occur also in measurements in the field. b) the frequency range required seems to extend to extremely low frequencies, with attendant complications as to the instrumentation necessary, not to mention the long time involved in obtaining the data.

2.3 Noise measurements

The major accomplishment has been the successful development at NBS of a special low noise potentiostat. This instrument has shown much better characteristics than commercial potentiostats whose noise level, as shown in fig. 5, is such that in many cases it can obscure the information sought.

The NBS potentiostat has a special amplifier for the detection of the a.c. current that runs through the test cell. The useful frequency range is from 10 mHz to 1 kHz. The noise current I_n generated by the potentiostat can be considered as the sum of I_{CV} caused by the control voltage, and I_A generated inside the a.c. amplifier

$$I_n = I_{CV} + I_A \quad (2)$$

By means of the circuit shown in fig. 6, the instrument can be calibrated, measuring the noise spectrum for various values of the resistor simulating the working electrode. Results are shown in fig. 7. The noise current is inversely proportional to the value of the resistor employed since it is

$$I_{CV} = V_{CV}/R \quad (3)$$

where V_{CV} is the noise voltage in the control voltage generator. V_{CV} can be measured directly, with the circuit in fig. 6, by turning the switch up and measuring directly the noise voltage across the resistor. The results are shown in fig. 8. The upper solid trace is V_{CV} which appears with the spectra shown in fig. 7. V_{CV} is of the order of $5 \cdot 10^{-8} V/\sqrt{\text{Hz}}$ but increases up to 100 nV/ $\sqrt{\text{Hz}}$ at very low frequency where flicker noise is predominant. The dotted line on fig. 8 indicates that a certain degradation in the quality of the signal occurs when a current near to maximum output of the potentiostat is drawn. The two peaks at 60 and 180 Hz are due to incomplete shielding from the a.c. power. They, however, can be reduced by better electromagnetic shielding, and are not very troublesome since they can easily be recognized as spurious signals.

Fig. 8 shows also the spectral amplitude when the potentiostat is disconnected. The noise found here is due to the amplifying and measuring circuits and represents the minimum detection level of the equipment in the present configuration. The potentiostat adds to that a noise which is only five times larger.

When the resistor simulating the working electrode is larger than a few $K\Omega$ the noise current does not increase anymore. As shown by equations (2) and (3), in these conditions the value of I_A , the noise generated by the a.c. amplifier is predominant. This is of the order of $3 \cdot 10^{-11} A/\sqrt{Hz}$.

In order to form an idea of the capabilities of the noise measurement system, some electrode systems have been investigated. As an example of a low noise electrode the deposition and dissolution of copper in copper sulfate has been tested. Results are shown in fig. 9. The noise levels are consistent with a reaction resistance of the order $20\Omega cm^2$, which can be calculated by combining equations (2) and (3):

$$R = \frac{V_{cv}}{I_n - I_A} = \frac{5 \cdot 10^{-8}}{I_n - 3 \cdot 10^{-11}} \quad (4)$$

Such a resistance is equivalent to an exchange current density of about $1 mA/cm^2$, close to that found in the literature. Higher noise, that is lower reaction resistance, is found when current is passing. These results are in agreement with the interpretation that the noise measurements in this case are equivalent to a wideband impedance measurement, from which one can derive the value of the reaction resistance.

A corroding system, aluminum in boric:borate solution, in the absence and in the presence of a small amount of NaCl, has also been

tested. Results are shown in fig. 10 and 11. The noise spectra of fig. 10 in the absence of NaCl show only minor changes by anodic polarization. The current is small, and changes are limited to an increase in noise at low frequencies and to a shift in the peak at about 600 Hz, probably due to a decrease of the electrode resistance. Only by strong cathodic polarization, when hydrogen evolution sets in ($i = -1 \text{ mA/cm}^2$), is the noise level drastically increased at all frequencies, as shown by the solid line in fig. 10. We have too little experience for the interpretation of this result; it is possible that the high noise is associated to the discrete nature of hydrogen bubble formation.

Fig. 11 shows the dramatic effect of the addition of 0.01 M NaCl, which is known to cause pitting. While the zero current spectrum is not affected, anodic polarization causes a steady increase in current, often in bursts, and an increase in noise levels of more than two orders of magnitude. The spectrum exhibits rather well developed peaks, as shown in fig. 12, but whether these features occur in a systematic way is not yet known.

2.4 Summary of the laboratory work

The objectives achieved in the past year can be summarized as follows:

a) Current-potential measurements on CCN wires have been carried out, showing the influence of the various environmental conditions.

b) Kinetic parameters, useful for the interpretation of the field polarization measurements, have been obtained from the analysis of the current-potential data.

c) Impedance measurements on CCN wires have been tested as to their suitability as a diagnostic tool in the field. The results have been negative.

d) The development of instrumentation for another possible corrosion detection method, the measurement of electrochemical noise, has been continued. A special potentiostat has been built at NBS and tested, with encouraging results.

e) Electrochemical noise measurements have been made on a number of electrodes, and experience in interpreting the experimental results is being accumulated.

3. Field Studies

During the first year specimens were prepared and buried at the outdoor NBS test site, and preliminary electrochemical measurements were made after burial. The results of this are described in the first annual report.

This year, our objective has been to bring the findings in the laboratory to bear on the measurements at the outdoor test site. This section will deal with this and other aspects of the studies.

Through the year, the experimental procedure was continuously being changed and improved. The main reason for these changes was to raise the signal to noise ratio of our measurements with the bulk of the interference being the background alternating current in the cable. In principle, the solution to the problem is simply to separate the dc signal of interest from the ac signal. In practice the difficulty is that the dc signal is less than 10 mV while the background signal is over three orders of magnitude larger or about 50 volts. Along with this ac voltage a dc component was discovered.

In addition, there are a number of "earth currents" at our test site which emanate from a variety of sources some of which we have identified. Three of these sources in decreasing order of importance are, 1. the grounding rod at the power supply transformer to the test site, 2. the steam generating plant for the entire NBS complex located about 200 meters north east of our test site, and, 3. the cathodic protection system in operation on the utilities distribution system for the NBS complex. Other sources of interference such as a high frequency ac signal coming from the NBS broadcasting system and a dc communication line that runs alongside our test site are intermittent, low power signals which are of little significance.

At the initial stages of the program, alternating current was not imposed on the buried cables. Thus, the electrochemical measurements during this period were satisfactory. The only interference in these measurements was the current from the grounding bar at the power supply transformer for the test site.

3.1 Experimental Procedure

3.1.1 Potential Measurements

Open circuit potential surveys are made of each specimen at the field site. This survey consists of making soil surface potential measurements at the intersections of an 18m x 2m grid at 1m intervals along the length of the buried cable using a Cu-CuSO₄ reference electrode. Each point on the grid is marked at the field site with a permanent aluminum marker imbedded in the ground. With these markers it is possible to make repeated measurements over several months at the same point. The survey allows one to rapidly and simply detect the changes that may occur along the length of the cable. It was from the potential survey measurements that the earth currents were first detected.

In an effort to determine the relative amount of earth current flowing on the NBS grounds compared to other sites, potential measurements between two like reference electrodes were made as shown in figure 13. The potential on the perimeter of the circle was measured with reference to the electrode located at the center of the circle. Considering the earth between the two electrode as a simple resistor, a qualitative evaluation of current flow can be surmised. This measurement was made at two sites in addition to the NBS site.

3.1.2 Soil Modification and Cable Inspections

As a result of the laboratory studies which indicated that the corrosion rate of the concentric neutral cable could be raised by increasing aeration in the presence of chlorides, the soil at the field test site was locally modified. An excavation was made on cables 3 and 4 that was 1 x 1m square and over 1m deep extending approximately 30 cm below both cables. While exposed, the 1 meter lengths of cable were visually examined. One of the cables was cleaned with distilled water prior to the inspection.

After visual inspection, the excavation was backfilled with a mixture of equal volumes of the soil removed and sand. As the layers of soil-sand mixture were added, a solution of sodium chloride was poured over each layer. A total of four kilograms of sodium chloride were added to the backfill material. Three months after the modification, the soil was qualitatively tested for chloride content and the soil resistivity measured at three locations at the site, and at three depths at each location. The chloride evaluation was made by taking 100 g of soil and mixing it with 200 ml of distilled water. After standing for 30 minutes the mixture was filtered so that a clear solution resulted. 1 ml of a saturated solution of silver nitrate was added to the filtrate causing any chloride to precipitate as silver chloride.

3.1.3 Polarization measurements

The circuit diagram being used for polarization measurements is illustrated in figure 14. This diagram can be thought of as two separate circuits with the section to the left of the specimen providing and measuring the current for polarization while the circuit to the right measures the resultant potential change of the specimen.

The section on the left has a DC power supply whose current output to the specimen is controlled by a voltage divider circuit not shown in the illustration. In addition to this voltage divider there is a variable resistor which also assists in current control. Two switches in parallel, as illustrated, can completely isolate the specimen from the current circuit. The normally open (N.O) switch is a push button microswitch used for intermittent current control. The on-off switch bypasses the N.O. switch when needed for longer term current applications. The output of the DC power supply is measured by a zero resistance ammeter. Notice that the ammeter is in parallel with a capacitor which serves as an AC filter for the ammeter, and allows most of the AC to travel to ground through the counter electrode without affecting the DC current measurement.

The section of the circuit shown to the right of the specimen in figure 14 is used to measure the potential of the specimen with respect to the Cu-CuSO_4 reference electrode. The potential is measured across a Wheatstone bridge which is used to measure and compensate for any IR error.

The high impedance voltmeter is isolated from the background AC by means of a two-pole low-pass filter circuit which reduces the 60 Hz signal by as much as a factor of 5000.

Measuring the corrosion rate of a finite length of a metallic member in an electrolyte such as soil is, in general, not difficult using techniques developed here and elsewhere (4). However, measuring the corrosion rate of what amounts to an infinite length of metal poses a special problem. The problem is that of not knowing how much of the metallic specimen surface is being polarized. If the surface area being polarized is not known, then corrosion current densities cannot be calculated.

Fortunately there may be ways to get around this problem. For example, polarization measurements can be made at several points along a cable. The positions of the electrodes would be changed for each measurement as illustrated in figure 15. The polarizability, the current necessary to polarize a section of cable 6 mV, of each section of cable would then be compared. The amount of current necessary to polarize a section of cable 6 mV is directly related to the corrosion rate of the section. Another approach is to distribute the current uniformly over a length of cable and then look for any discontinuities in potential along the cable. Such discontinuities would warrant closer inspection.

In order to determine current distribution, current was applied to a cable from a counter-electrode driven into the ground at a given distance as shown in figure 16. Potential measurement were then made over the length of the cable. The change in potential with and without polarizing current applied was then plotted for each point along the length of the cable.

3.2 Results and Discussion

A considerable amount of time and effort has been expended in improving our ability to do measurements in the presence of interfering signals. As mentioned earlier the sources of interference have been numerous. Each had to be identified and eliminated by either removing the source or filtering out its effects.

3.2.1 Potential Measurements

The first evidence of a problem appeared in the open circuit potential measurements of the cables. The effect of the AC signal on the potential readings of cable 3 is illustrated in figure 17

which shows that with AC the potential around position 10 of cable 3 is over 50 mV more noble than the end of the cable. Because this variation in potential with position did not improve with time, it was investigated further. Open circuit potential measurements made along a line perpendicular to the length of the cable indicated an increase in potential as one moved a short distance towards one source of ac, cables 1 and 2, as shown in figure 18. As several meters were traversed with the potential readings, a dramatic increase in potential developed immediately over cables 1 and 2 as figure 17 shows. An even greater variation in potential (not shown) occurred as the measurements were extended beyond cables 1 and 2 and approached the area of the grounding rod for the field site power station. It became apparent that this interference could not be tolerated, and had to be removed before the electrochemical measurements could proceed. Thus, the grounding rod was moved over 40 m away from the nearest cable reducing the effect of this source of interference.

Once this massive interference was removed, it became possible to analyze and correct the other sources. Using a portable oscilloscope it was found that along with the ac signal there was a DC component. This component was coming through a common ground that connected our site to a distant building housing large power transformers for the entire NBS site. This dc component was easily removed by inserting an isolation transformer at our field site which filtered out all unwanted dc signals from the transformer station. Moving the ground rod and introducing the isolation transformer into the circuit resulted in reducing the total effect of interference by an order of magnitude as shown in figure 19.

The oscilloscope also revealed an intermittent high frequency ground signal which was eventually found to come from the NBS fire and security broadcasting station whose antenna is located in the same building that houses the power transformers and with whom we have a common ground. This is a low order signal that would have negligible effect on our site.

Using two reference electrodes in a circle it was possible to trace earth current sources. As the field site was traversed it was found that a current source came from the direction of the steam generating plant located over 100 m from our field site. A second possible source of this earth current is the NBS cathodic protection ground bed located over 1000 m from our test site. The maximum potential measured between the reference electrodes 5 m apart was 30 mV which for our soil results in a maximum current of approximately 0.3 mA assuming a soil resistivity of 10,000 Ω cm. Relative earth current measurements were made at two other sites as figure 20 illustrates. At Lock Raven, north of Baltimore, Maryland, the earth current calculated was approximately 0.8 mA assuming a soil resistivity of 15,000 Ω cm. The ocean beach at Dam Neck, Virginia, resulted in the lowest earth current at 0.06 mA with a soil resistivity of 20,000 Ω cm. On the basis of these few measurements it was judged that the earth currents at the NBS site were typical of those found in this region. Since little can be done about these currents short of shielding the entire field site with a buried conducting barrier, and because they are expected to exist to some degree at all locations, it was decided to monitor, but not eliminate these low order earth currents.

Through the combination of the ac filtering system described earlier, the removal of the grounding rod from the vicinity of the test site, and the incorporation of the isolation transformer, all sources of interference were reduced to a tolerable level. Figure 21 illustrates the potential of cable 3 with and without ac on cables 1 and 2 with the filtering system in use. Similar data on cable 1 which has the ac signal imposed on it are shown in figure 22. The instability in the potential readings after 8 days is clearly evident in this figure. Three weeks later the potential stabilized and has remained relatively unchanged for the first three months.

3.2.2 Soil Modification and Cable Inspection

The visual inspection of the exposed cables showed that some loss of the tinning had occurred. On some areas of the wire, the copper was clearly visible through the coating. This is not necessarily significant since the coating was extremely thin to begin with. Thus, it was decided that little, if any, attack had developed on the concentric neutral wires during the eleven months of burial.

The chloride content evaluation made 3 months after the soil was modified revealed that all soil samples contained some traces of chloride, but only the intentionally modified soil contained significant concentrations detectable by the addition of silver nitrate to the aqueous extract of the soil.

The soil resistance measurements of samples taken from the same areas indicated that the resistivity of modified soil averaged 3,300 Ω cm from 0.5 to 1 m below the surface while other soil samples located away from the modified soil, but at the same depth, had soil resistivities that averaged almost 12,000 Ω cm. Clearly the soil modification was

still effective after 3 months. However, electrochemical measurements indicate that in the area of the soil modification there has been no discernible effect on the potential of the cables as shown in figure 23

3.2.3 Polarization Measurements

As indicated earlier, the initial polarization measurements were made at four points along each cable. Figure 24 is a plot of the current necessary to polarize the cable 6 mV, the polarizing current, for cables 3 and 4 at three different periods of time. The polarizing current for the cables has increased slightly and uniformly with time. Of particular interest is the fact that no significant change in current is observed where the soil is modified. There may be two reasons for this lack of reaction at that section of the cable. First, during this period the weather has been unseasonably dry. Second, because of low diffusion rates in soil, it may take more time for the cable to respond to the change in its environment.

Imposing an ac signal between cables 1 and 2, on the other hand, has had a large effect on the polarizing current. The initial polarization measurements indicated that the polarizing current of cable 1 was comparable to cables 3 and 4. Since applying the ac the polarizing current of cable 1 has been rising steadily as shown in figure 25. In particular note the relatively high polarizing current around position 12 after approximately 2 months.

In order to evaluate the distribution of current over the cable during polarization, the change in potential over the length of the cable was measured as current was applied from a vertical steel rod in the ground. The distance of the current source was varied from

0.5 m to 1 m. The resulting data, illustrated in figure 26, indicate that from a distance of 1 m the current is distributed over the 15 m cable with little concentration of current in the vicinity of the source located at position 5. As the current source (counter-electrode) is moved to within 0.5 m of the trench the current distribution begins to show a distinct concentration around the source. When a current of 900 mA is applied and at a distance of 0.5 m, 85% of the current is concentrated along 9 m of the 15 m cable. As the current is increased the distribution becomes more uniform. This type of information which describes the current distribution during polarization is necessary for corrosion rate determinations.

3.3 Summary of Field Studies

- a) the electrical interference problems have been eliminated.
- b) the soil has been locally modified around the set of cables, that has no ac signal applied
- c) visual examination of a section of cable without ac revealed little corrosion after 11 months of burial.
- d) polarization techniques are now being used in the field site to evaluate the extent of corrosion on the cables.
- e) these measurements indicate that the corrosion rate of the cables with an imposed ac are corroding at a substantially higher rate than those without ac.

4. Plans For Next Year

4.1 Laboratory Studies

- 1) Comparison between polarization measurements and weight losses
- 2) Analysis of polarization measurements in the presence of large ac signals

- 3) Noise measurements on Copper and tinned Copper
- 4) Work on overcoming problems arising from taking noise measurements in the field

4.2 Field Studies

- 1) Correlation of the electrochemical data with careful visual examination of the cables in the field
- 2) Evaluation of the polarization techniques and their distribution of current on longer cable in the field and application of these techniques to real cables
- 3) Evaluation of the influence of the carbon impregnated polyethylene on the distribution of current
- 4) Modification (locally) of the soil on a set of cables with ac
- 5) Evaluation of the noise technique on cables in the field.

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- Fig. 6. Circuit for noise measurements under potentiostatic conditions.
- Fig. 7. Effect of simulator resistance on noise current.
- Fig. 8. Noise voltage across simulator resistor.
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- Fig. 12. Peaks in noise voltage for Al in boric + borate + NaCl.
- Fig. 13. Earth current measurements.
- Fig. 14. Circuit diagram for polarization measurements.
- Fig. 15. The four positions for polarization measurements.
- Fig. 16. Graphic positions of counter & reference electrodes with respect to the cable.
- Fig. 17. The effect of ac on the potential readings.
- Fig. 18. The effect of ac on the potential readings.
- Fig. 19. The results of moving the ground rod and introducing the isolation transformer.
- Fig. 20. Earth current measurements at Loch Raven, MD and Dam Neck, VA.
- Fig. 21. The effects of stray currents on potential.
- Fig. 22. Stabilization of the dc potential.
- Fig. 23. The effects of modification of soil on potential.
- Fig. 24. Polarization of cables 3 and 4 without ac.

Fig. 25. The current produced by polarizing cable 1 to 6 mV.

Fig. 26. Distribution of current along cable.

Table I. Parameters obtained from polarization measurements on tinned Cu wire. Cells without ac signal.

Solution	2% Na ₂ SO ₄						2% Na ₂ SO ₄ + 1% NaCl							
	460	1150	1900	4300	5000	6700	9000	460	1150	1900	4300	5000	6700	9000
time, h														
Atmosphere O ₂	o.c.p., mV vs NHE	+246	+230	+265	+282	+291	+275	+90	+153	+115	+180	+183	+147	+185
	i _{corr} , μA/cm ²	0.7	0.3	0.8	3	1.7	0.4	2.5	4.0	3.5	5	2.5	0.5	0.1
	B, mV	7	17	21	100	80	--	--	39	40	12	10	25	7
	b _a , mV/dec	20	55	60	240	186	--	--	90	90	50	35	80	20
	b _c , mV/dec	75	150	300	∞	∞	large	large	∞	∞	80	65	300	80
Fit	fair	fair	good	fair	good	no	no	good	good	fair	poor	fair	poor	
Atmosphere N ₂	O.C.P., mV vs NHE	+202	+140	+143	+100	+100	+90	+73	+75	+57	+80	+77	+63	+72
	i _{corr} , μA/cm ²	0.35	0.5	0.07	0.2	0.1	0.08	0.8	0.75	0.5	0.43	1.4	0.12	0.33
	B, mV	38	45	22	29	23	18	23	20	20	15	30	14	16
	b _a , mV/dec	100	120	70	110	80	60	60	60	60	50	70	45	50
	b _c , mV/dec	∞	∞	200	170	170	150	∞	180	210	120	∞	100	170
Fit	fair	fair	good	poor	fair	good	good	good	good	good	fair	good	fair	

Table 11. Parameters obtained from polarization measurements on tinned CCN wire. Cells with ac signal superimposed.

Solution		2% Na ₂ SO ₄				2% Na ₂ SO ₄ + 1% NaCl			
Time, h		1600	2400	4200	6700	1600	2400	4200	6700
Atmosphere O ₂	o.c.p. vs NHE	+275	--	+260	+267	+170	+200	+230	+225
	I _{corr} , μA/cm ²	0.35	--	0.25	0.25	3	2	0.1	0.4
	B, mV	21	--	16	17	40	20	8	11
	b _a , mV/dec	70	--	38	38	--	80	25	30
	b _c , mV/dec	160	--	600	400	--	120	70	100
	Fit	good	--	good	good	poor	fair	fair	fair
Atmosphere N ₂	o.c.p. vs NHE	+120	+90	+75	+120	+35	0	+40	+45
	I _{corr} , μA/cm ²	0.4	0.2	0.1	0.15	0.14	0.2	0.1	0.3
	B, mV	--	--	--	--	17	--	15	25
	b _a , mV/dec	--	--	--	--	60	--	55	60
	b _c , mV/dec	--	--	large	large	110	--	120	∞
	Fit	no	no	no	poor	fair	poor	fair	fair

Table III. Real (Z') and imaginary (Z'') values in $\Omega \cdot \text{cm}^2$ of the electrode impedance for tinned CCN wire in 2% Na_2SO_4 with nitrogen atmosphere

$t, h \rightarrow$ $v, \mu z \downarrow$	a.c. signal				No a.c. signal									
	1554		2280		3330		4299		5333		6120		8503	
	Z'	Z''	Z'	Z''	Z'	Z''	Z'	Z''	Z'	Z''	Z'	Z''	Z'	Z''
5	242.5	638	383.7	1233	361	889	217	817	438	1633	521	1477	124	569
8	210.5	457	318	795	274	630	174	538	373	1075	408	953	111.4	405
10	174	362	295	663	247	521	145	451	306	893	354	817	88.5	289
40	79.3	120	121	240	114	188	51.3	145	127	304	135	270	40.8	112.3
80	49.9	83.1	87.0	137	81.7	112	39.7	81.7	78.6	172	81.1	165	25.5	68.1
100	45.1	71.2	79.0	116	73.5	95.3	35.0	67.7	68.5	145	70.8	142	20.4	51.1
560	19.0	23.7	39.5	39.5	37.6	32.9	24.0	19.2	33.0	41.1	31.3	40.8	10.2	15.3
1 K	14.8	14.5	31.4	25.0	28.8	21.9	9.9	10.6	26.8	24.2	24.8	24.2	8.5	8.2
5 K	10.9	3.3	17.9	15.3	16.9	14.6	11.7	4.1	17.1	13.5	15.6	13.3	7.5	2.0
10 K	10.6	1.1	10.28	12.4	9.68	12.4	11.0	1.1	10.2	11.7	9.47	11.5	7.5	0.2
50 K			3.54	3.54	1.95	3.46			3.16	3.69	1.82	3.63		
100K			2.70	1.43	1.41	1.73			2.63	1.45	1.24	1.66		

Table IV. Real (Z') and imaginary (Z'') values in $\Omega \cdot \text{cm}^2$ of the electrode impedance for tinned Cu wire in 2% N_2SO_4 with oxygen atmosphere

t, h → v, Hz ↓	a.c. signal				No a.c. signal							
	1557	2561	3329	4299	5333	6123						
	Z'	Z''	Z'	Z''	Z'	Z''	Z'	Z''				
5	1659	2552	844	1062	2859	2178	877	1098	3012	3948	2723	3812
8	1139	1856	659	764	2461	1866	852	877	2568	2979	2477	2635
10	942	1571	606	685	2299	1731	752	777	2312	2594	2147	2356
40	327	607	255	316	1002	950	475	427	852	1328	796	1156
80	159	371	166	222	745	796	432	237	451	852	437	771
100	139	325	143	191	642	744	210	189	371	718	351	664
500	40.8	96.1	51.0	69	167	308	26	60	74.3	220	71.5	204
1 K	24.8	56.9	33.2	43.4	85	167	22.8	38.0	39.6	124	38.1	112
5 K	11.8	12.7	15.0	18.6	11.2	58.9	10.7	7.8	11.1	33.4	9.5	50
10 K	10.4	7.4	8.7	13.2	1.83	29.6	9.9	3.2	5.8	18.9	4.2	16.9
50 K			2.6	3.4	0.87	4.38			3.8	3.85	1.0	3.5
100K											0.96	1.9

Table V. Real (Z') and imaginary (Z'') values in $\Omega \cdot \text{cm}^2$ of the electrode impedance for tinned CCN wire in 2% Na_2SO_4 1% NaCl with nitrogen atmosphere

t, hV	a.c. signal				No a.c. signal			
	1556	2544	3329	4299	5333	2124	8521	
ω, Hz	Z'	Z''	Z'	Z''	Z'	Z''	Z'	Z''
5	40.8	268	167	472	176	271	240	626
8	32.2	170.8	68.1	300	105	78.7	183	419
10	36.0	132.1	59.9	245	70.6	171	155	349
40	14.2	39.6	30.0	76.2	50.1	67.7	66.4	115
80	12.0	21.6	24.5	40.6	32.4	34.9	48.5	66.4
100	8.4	17.3	23.1	32.7	17.5	30.5	43.6	60.0
200								
400								
500	7.0	4.8	16.9	9.53	9.3	8.8	25.5	17.9
1K	6.3	2.4	15.0	6.53	8.9	6.9	23.0	13.5
3K								
5K	5.0	0	10.2	6.71	6.3	0.9	13.6	10.1
10K			6.21	6.51	9.48	10.0	7.89	9.86
20K								
50K			1.03	2.18	3.01	3.01	2.90	2.90
100K			0.53	0.50	2.19	1.26	0.88	1.46

Table VI. Real (Z') and imaginary (Z'') values in $\Omega \cdot \text{cm}^2$ of the electrode impedance for tinned CCN wire in 2% Na_2SO_4 , 1% NaCl with oxygen atmosphere

t, h \rightarrow	a.c. signal				No a.c. signal							
	1537	2544	3329	4275	5309	6124	Z'	Z''				
ν , Hz \downarrow	Z'	Z''	Z'	Z''	Z'	Z''	Z'	Z''				
5	204	255	3063	2552	2422	2000	609	456	1233	822	817	735
8	158	183	2351	2129	1906	1661	906	229	1027	632	650	572
10	139	158	2030	1980	1688	1525	647	227	1027	579	598	520
40	72.9	68.1	749	1063	735	898	394	219	580	369	279	254
80	58.3	46.2	382	693	422	653	312	209	442	286	205	180
100	52.3	41.3	287	597	351	572	288	209	395	282	155	160
500	26.6	25.4	52.8	178	77.2	188	170	162	160	189	96.4	76.1
1K	21.1	18.2	28.8	96.1	27.2	100.7	44.8	74.7	80.1	140	68.9	63.8
5K	7.62	4.90	8.41	25.2	4.96	26.2	13.1	17.7	8.79	42.4	16.3	35.4
10K	7.24	2.17	4.32	13.1	1.94	13.4	11.3	10.1	2.43	21.4	4.59	20.3
50K			2.08	2.97	.77	2.94			1.91	3.81	0.87	4.34

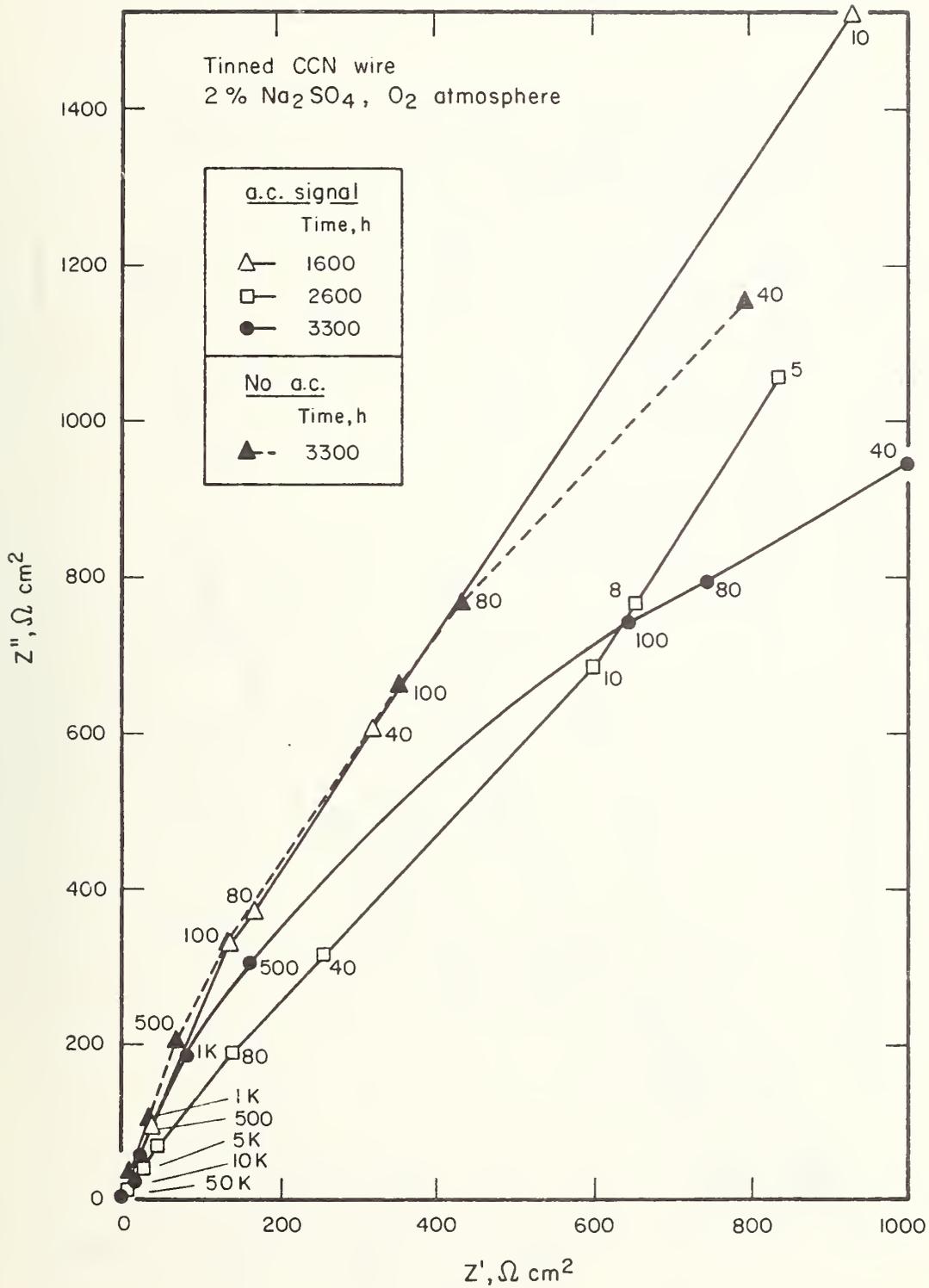


Fig. 1. Z'' vs Z' for CCN in O₂ atmosphere. Frequency as parameter.

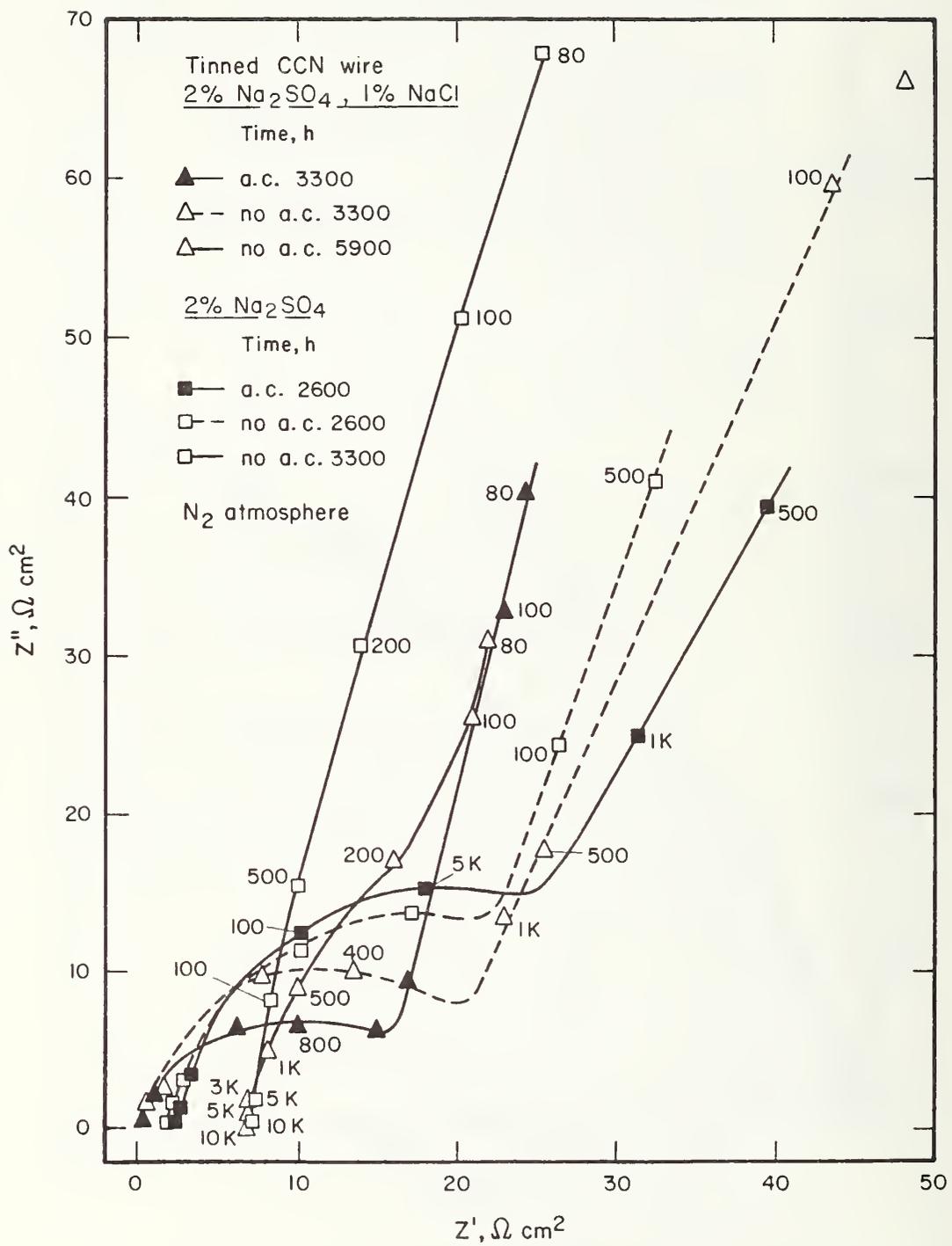


Fig. 2. Z'' vs Z' for CCN in N₂ atmosphere. Frequency as parameter.

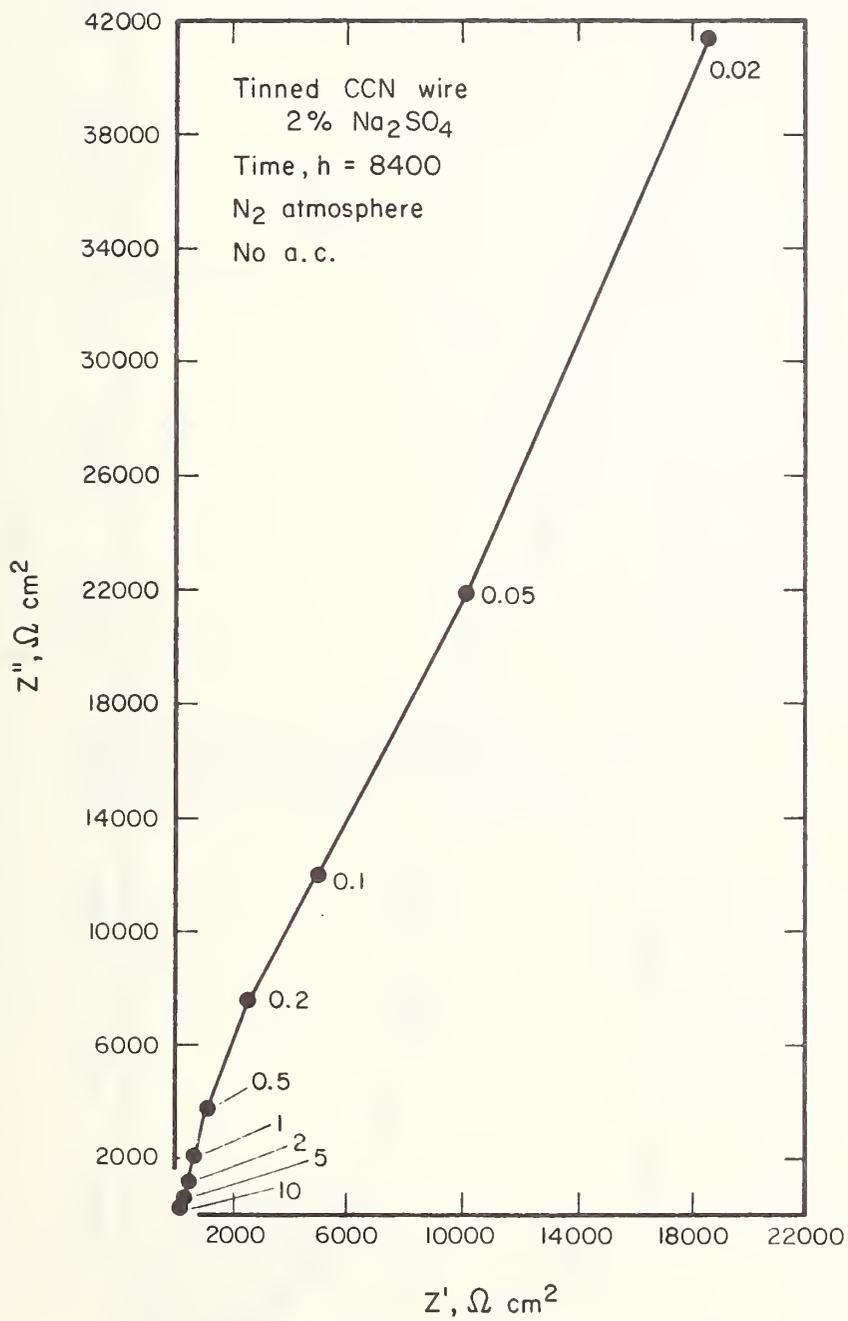


Fig. 3. Z'' vs Z' for CCN in N₂ atmosphere at low ν . Frequency as parameter.

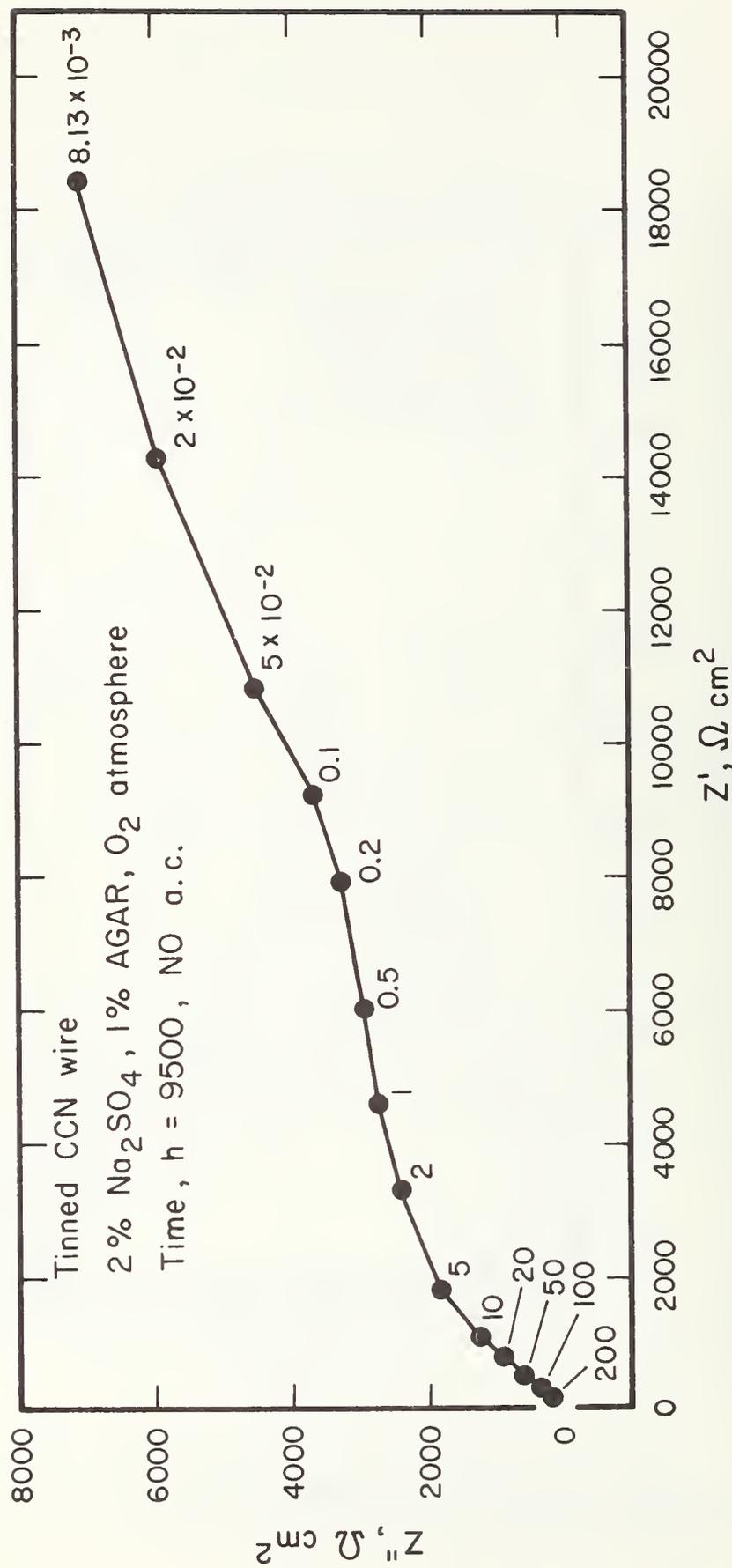


Fig. 4. Z'' vs Z' for CCN in O₂ atmosphere at low ... Frequency as parameter.

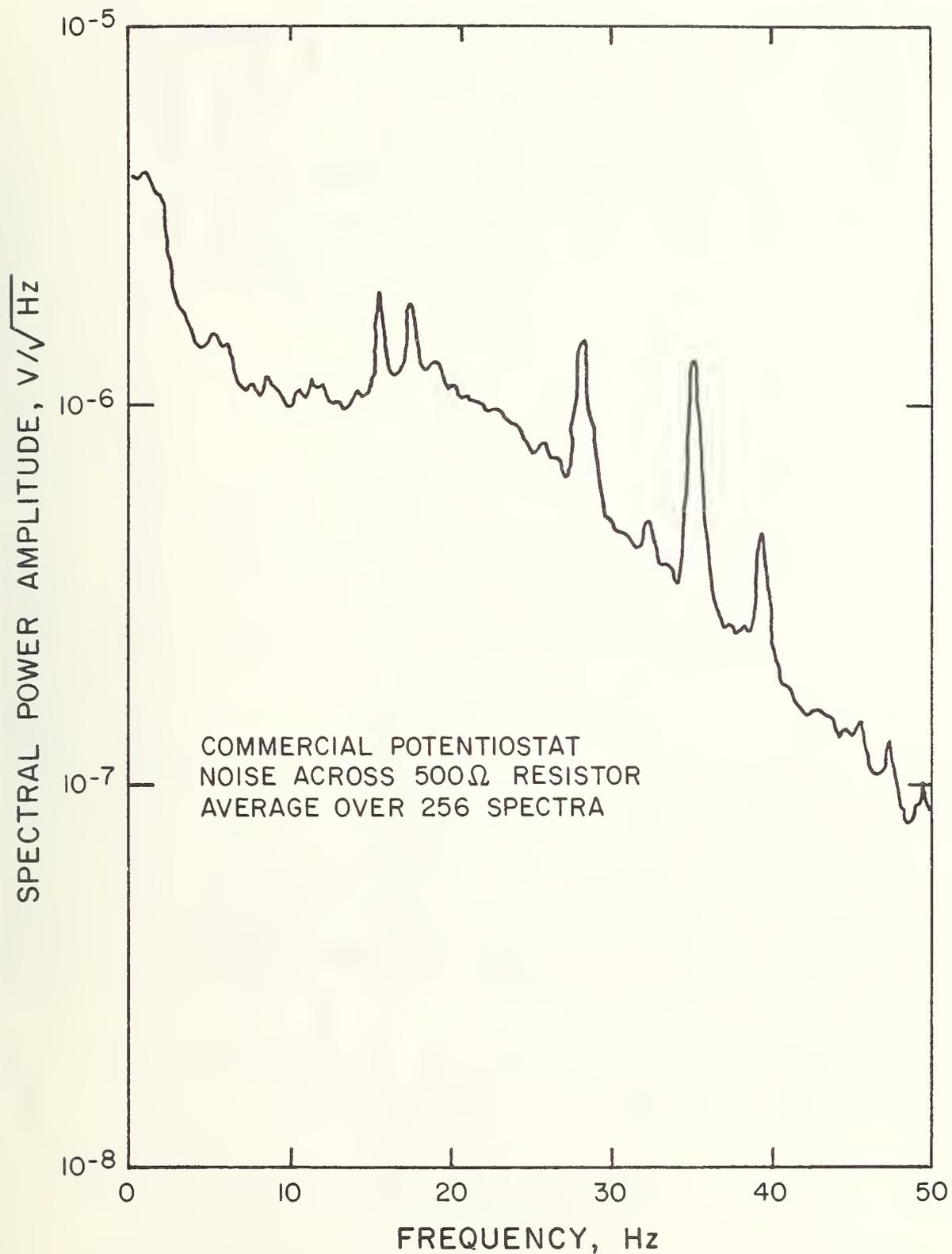
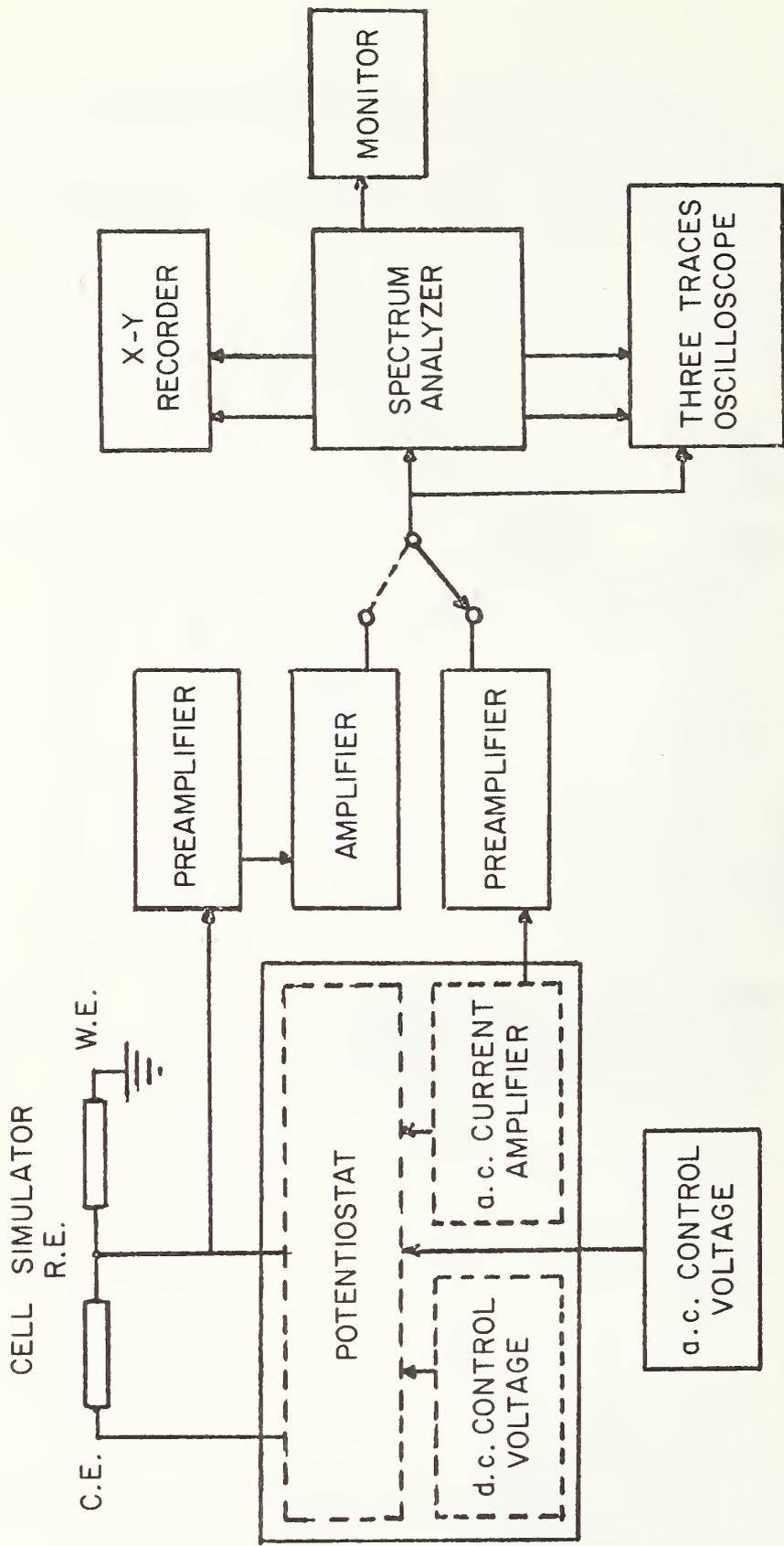


Fig. 5. Noise spectrum of commercial potentiostat.



POTENTIOSTAT TESTING CIRCUIT

Fig. 6. Circuit for noise measurements under potentiostatic conditions.

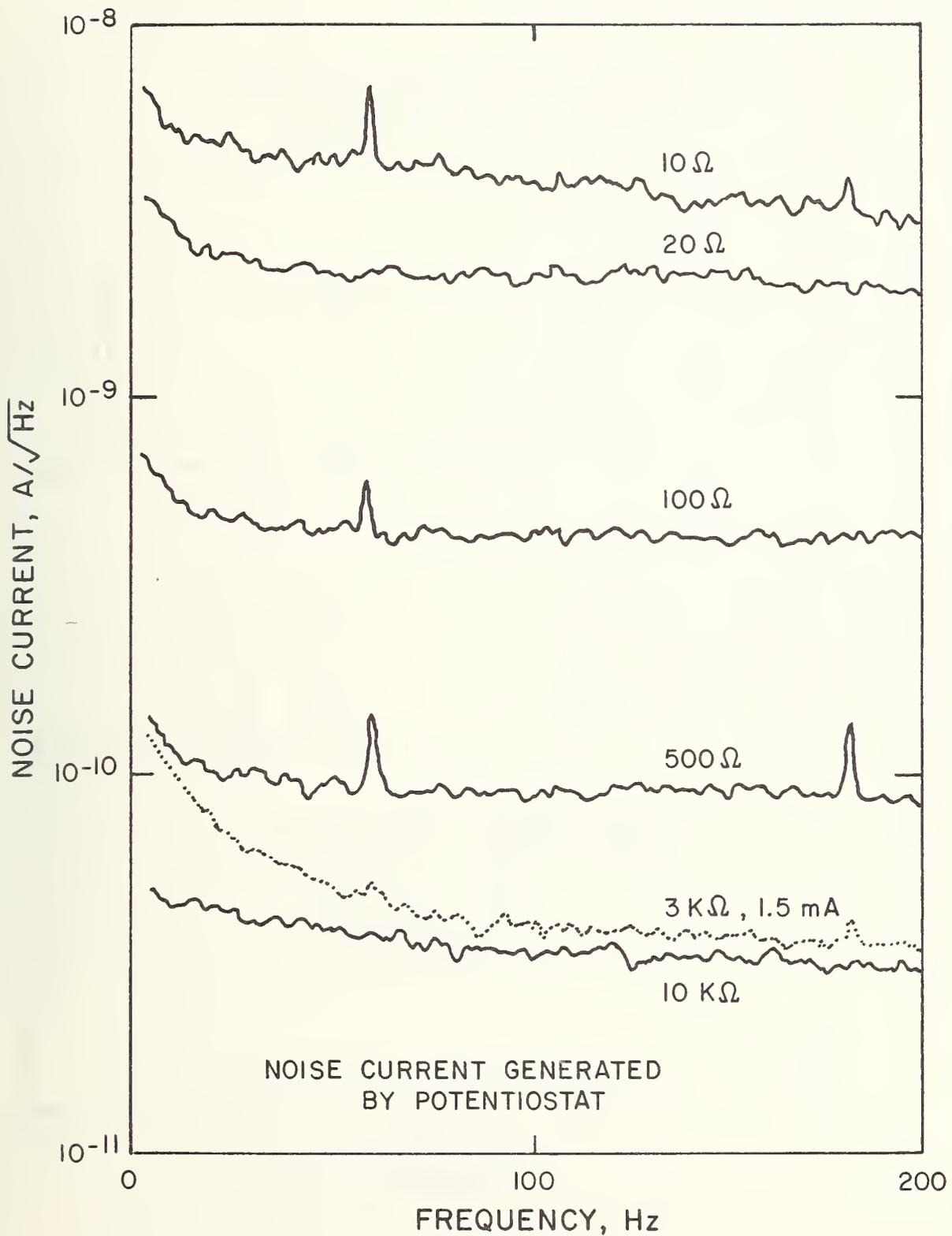


Fig. 7. Effect of simulator resistance on noise current.

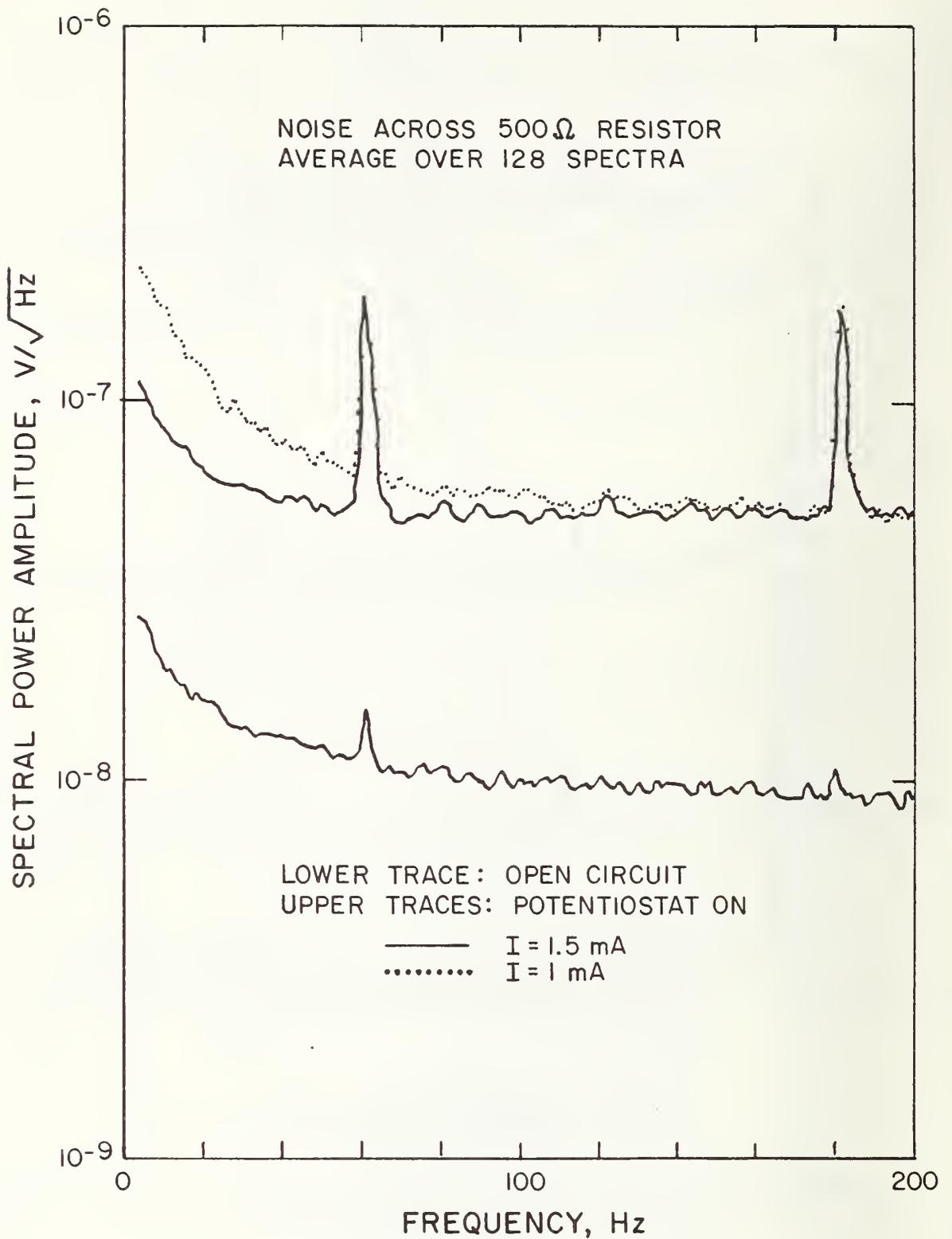


Fig. 8. Noise voltage across simulator resistor.

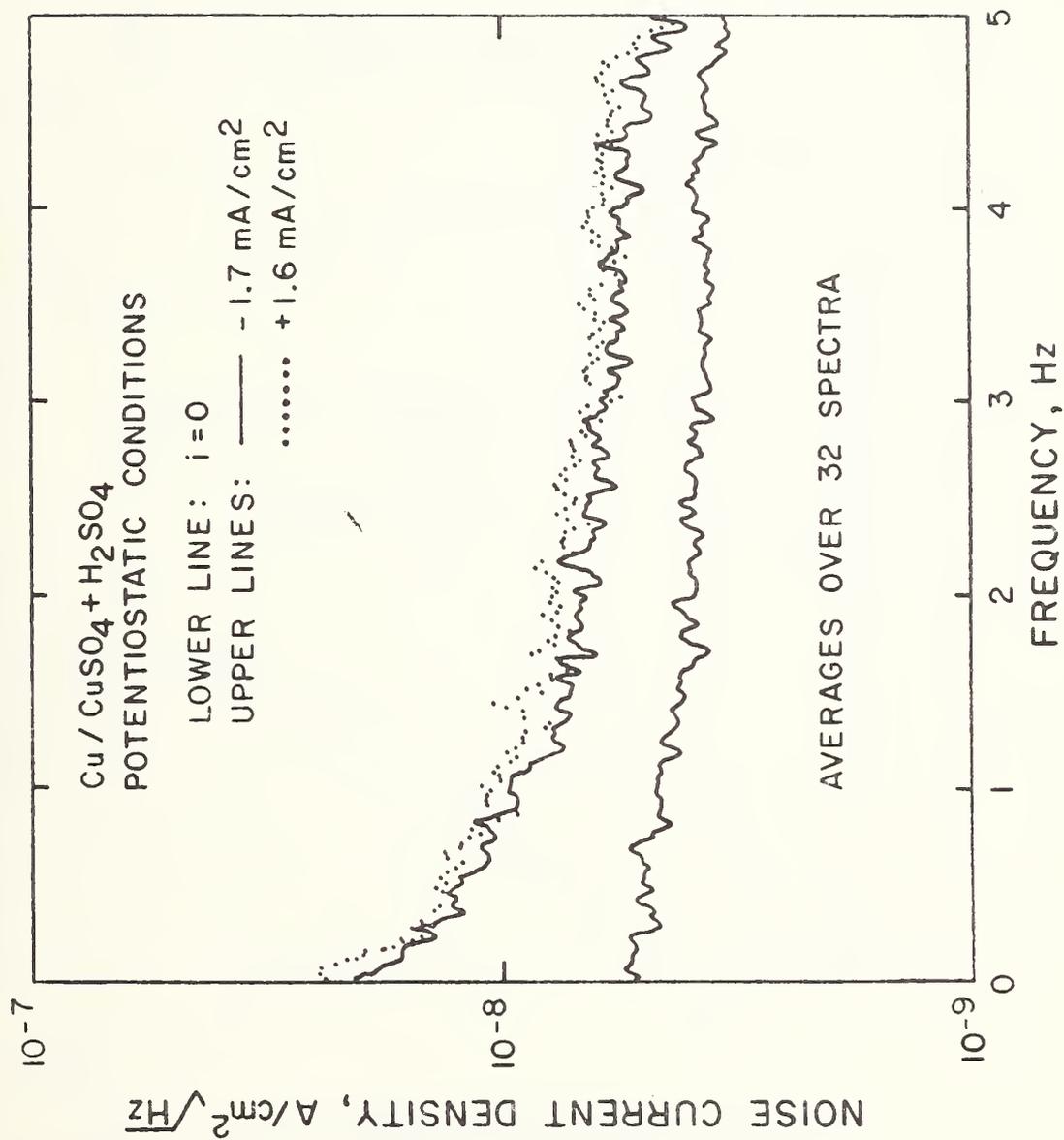


Fig. 9. Noise spectrum of Cu in acidified CuSO_4 .

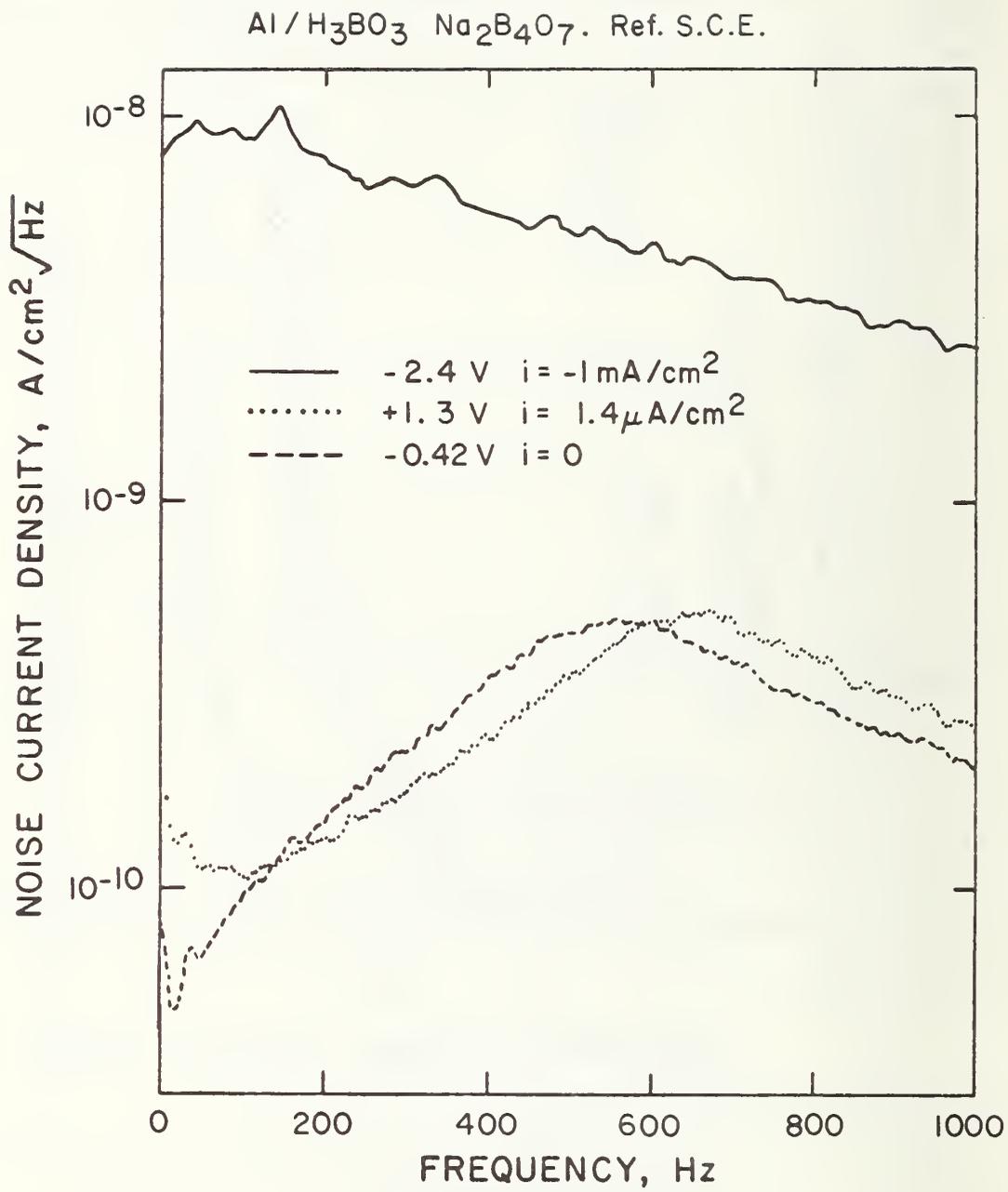


Fig. 10. Noise spectrum of Al in H₃BO₃: Na₂B₄O₇.

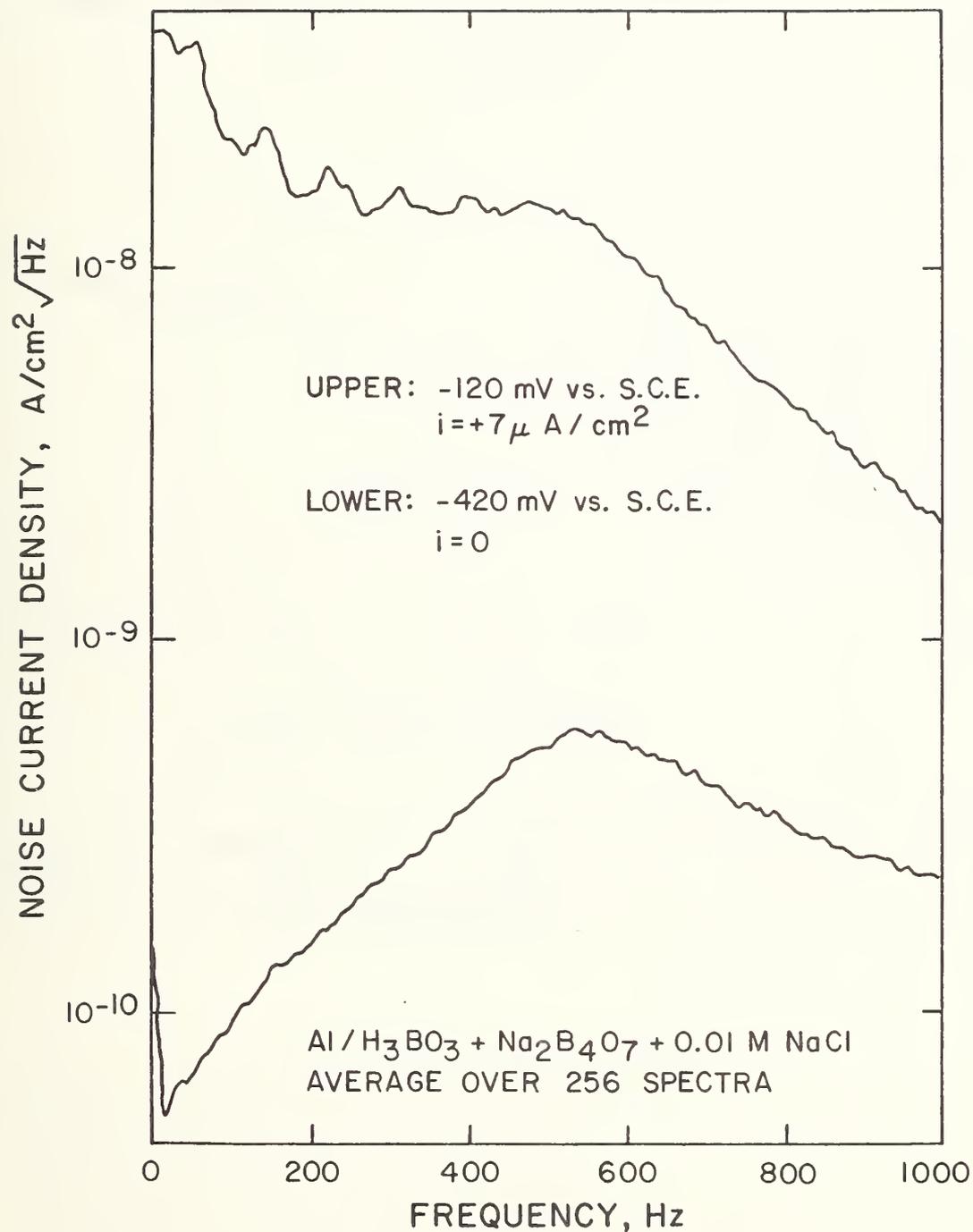


Fig. 11. Noise spectrum in Al in H_3BO_3 : $Na_2B_4O_7$ with 0.01 M NaCl.

Al/H₃BO₃ + Na₂B₄O₇ + 0.01 M NaCl

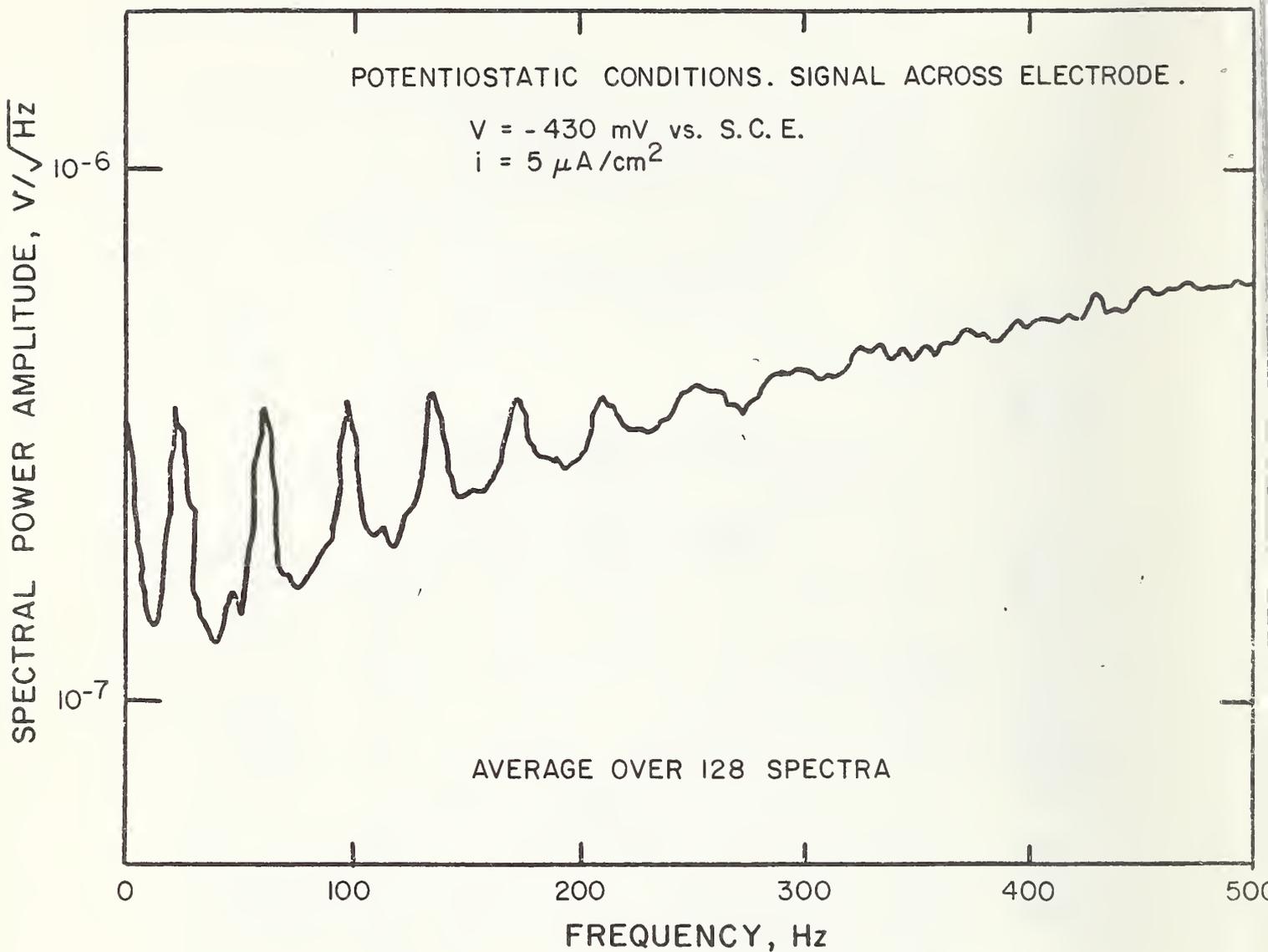


Fig. 12. Peaks in noise voltage for Al in boric · borate + NaCl.

**EARTH CURRENT MEASUREMENT
(POTENTIAL BETWEEN TWO Cu-CuSO₄ ELECTRODES)**

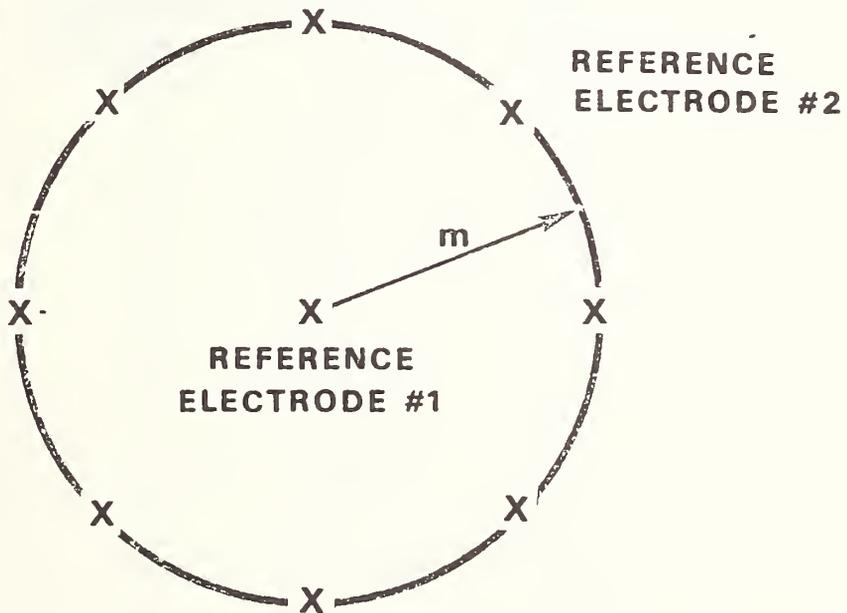


Fig. 13. Earth current measurements.

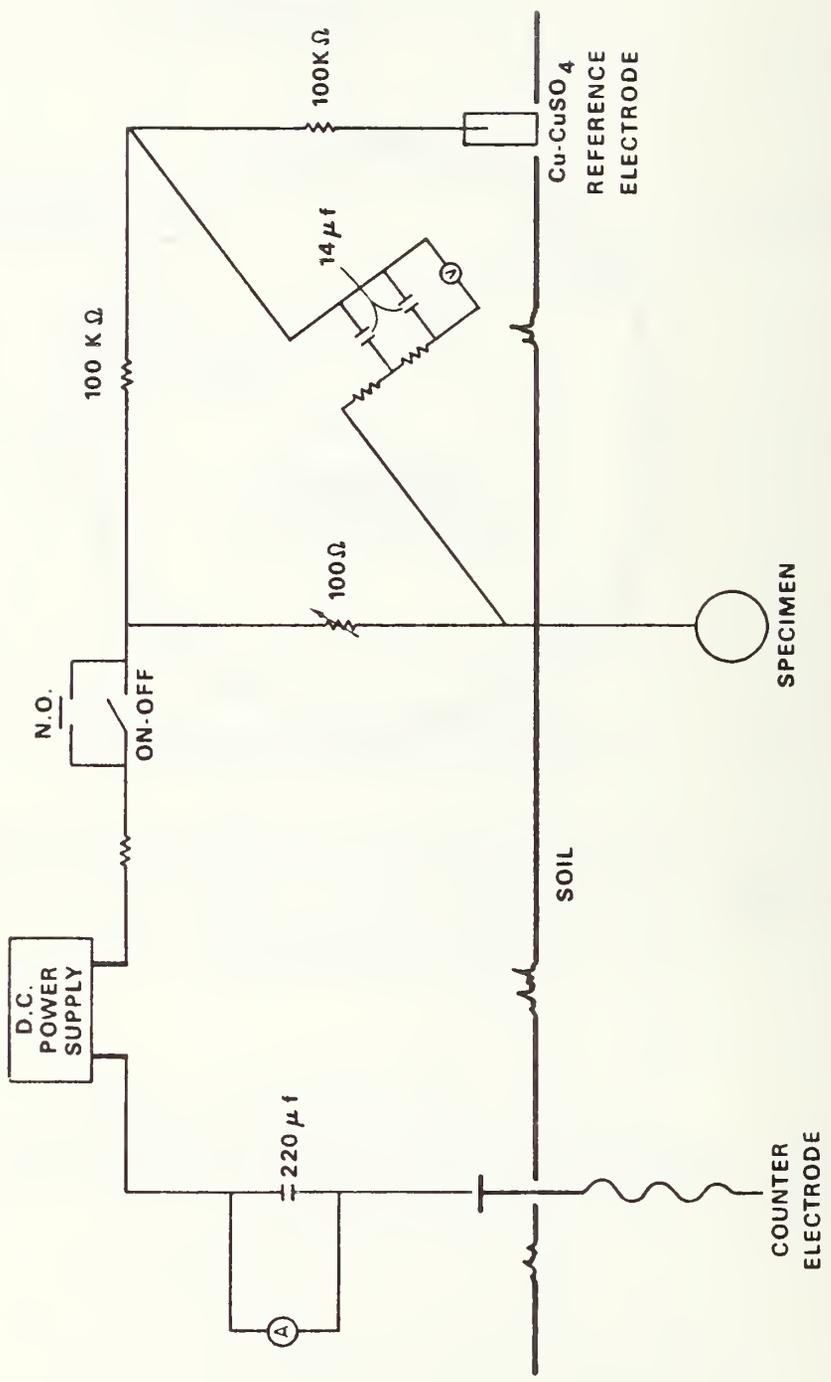


Fig. 14. Circuit diagram for polarization measurements.

GEOMETRY OF POLARIZATION ELECTRODES TOP VIEW

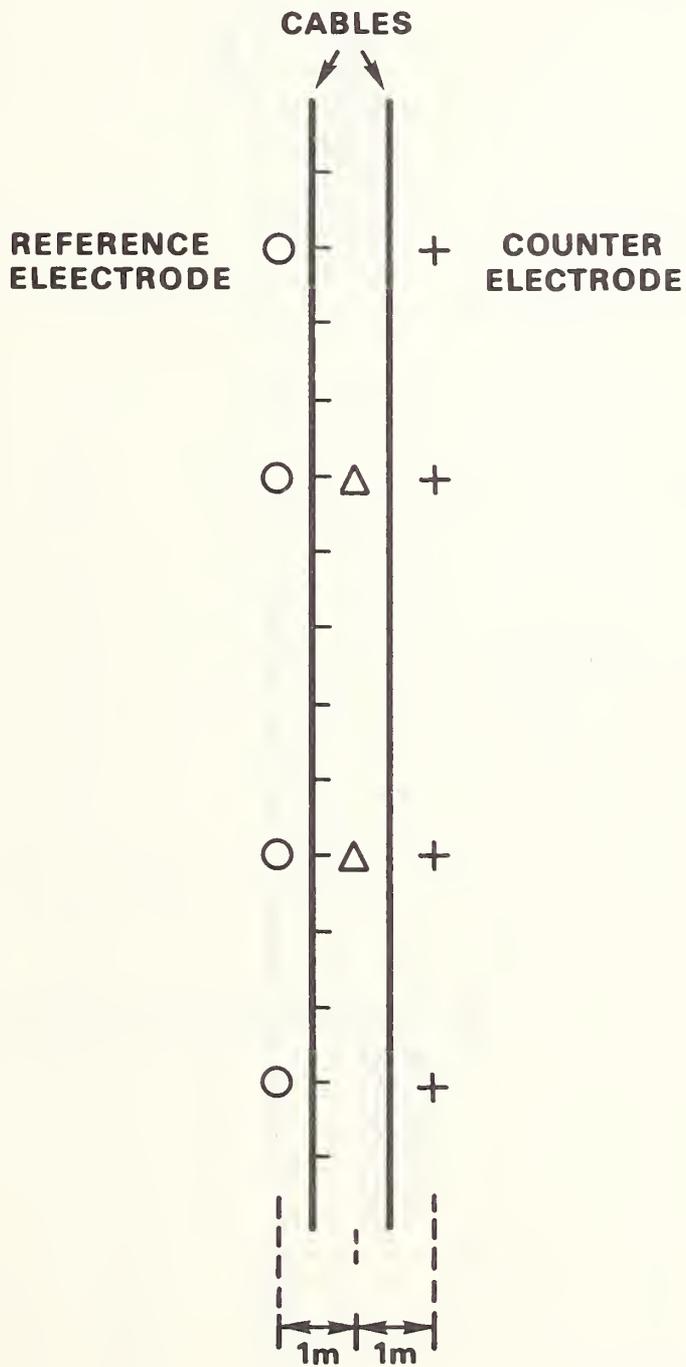


Fig. 15. The four positions for polarization measurements.

GEOMETRY OF POLARIZATION ELECTRODES END VIEW

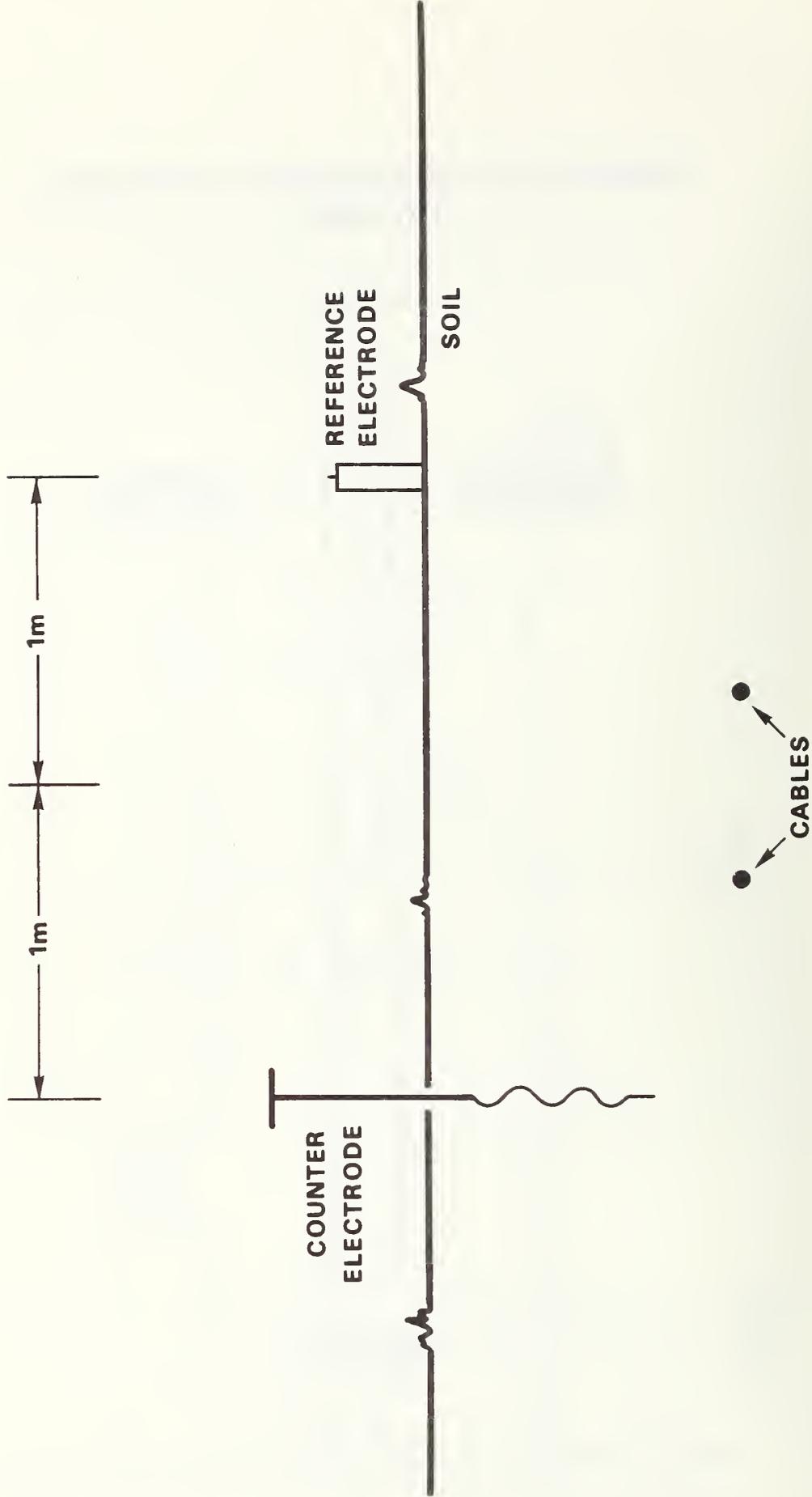


Fig. 16. Graphic positions of counter & reference electrodes with respect to the cable.

CABLE 3
DATA

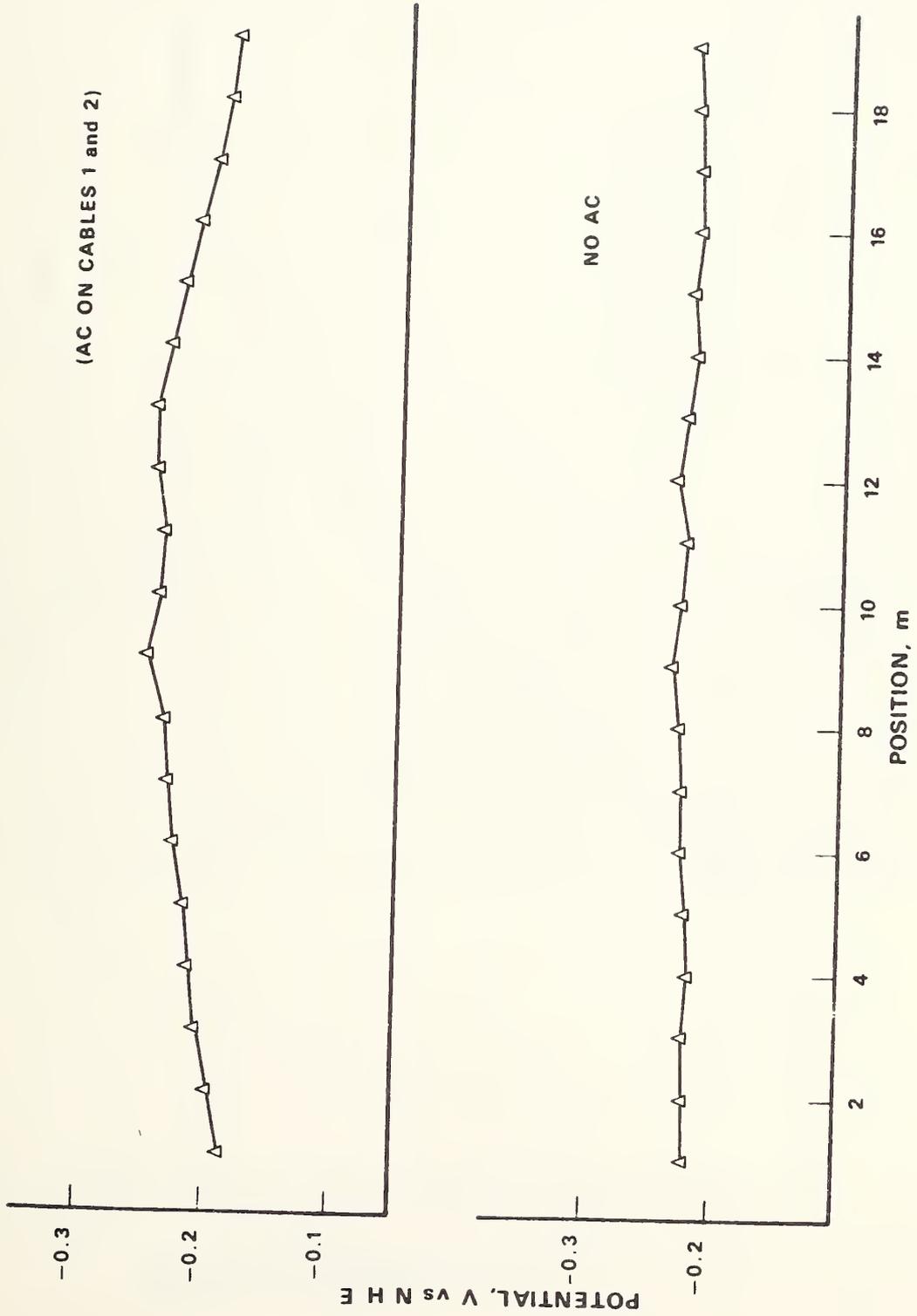


Fig. 17. The effect of ac on the potential readings.

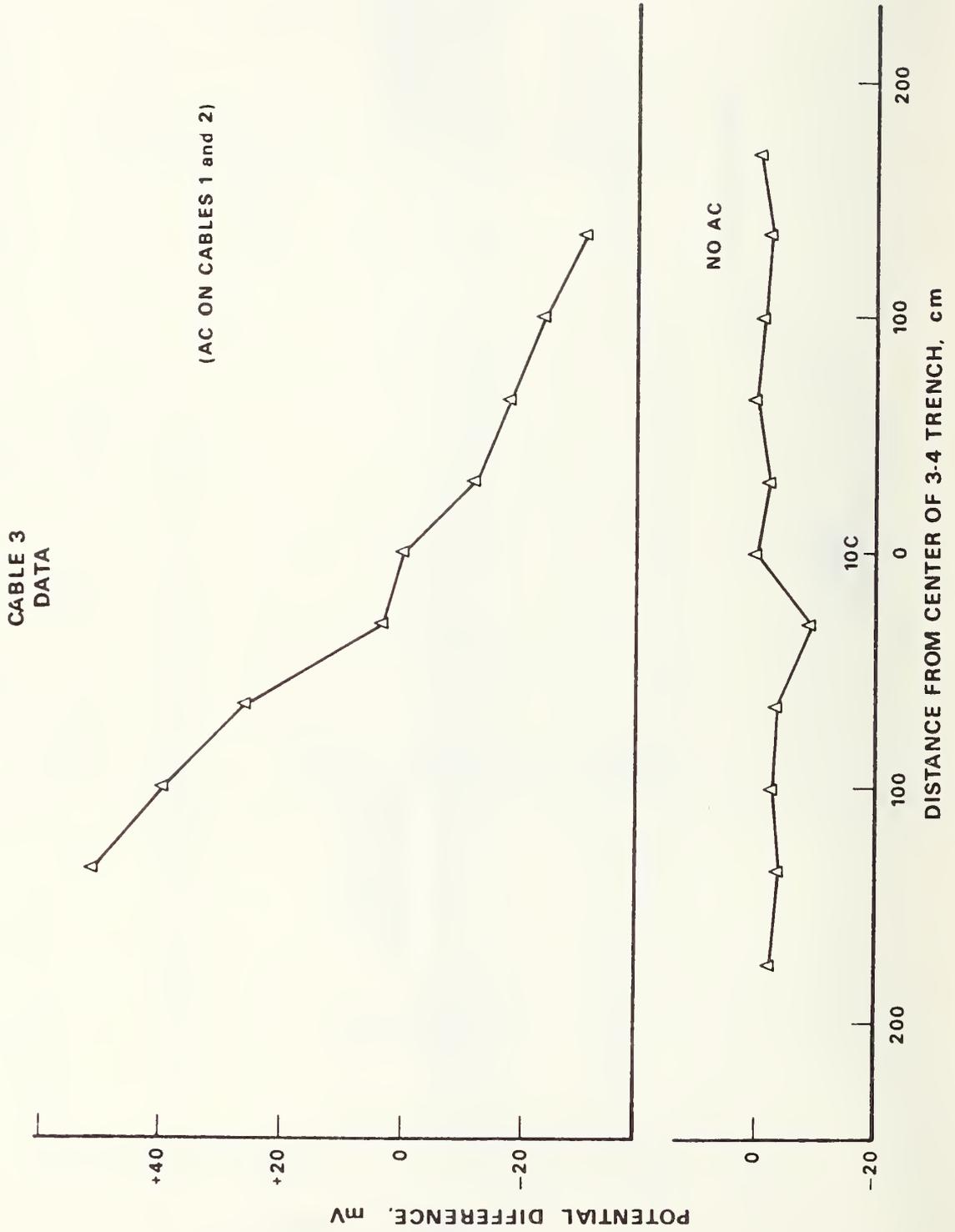


Fig. 18. The effect of ac on the potential readings.

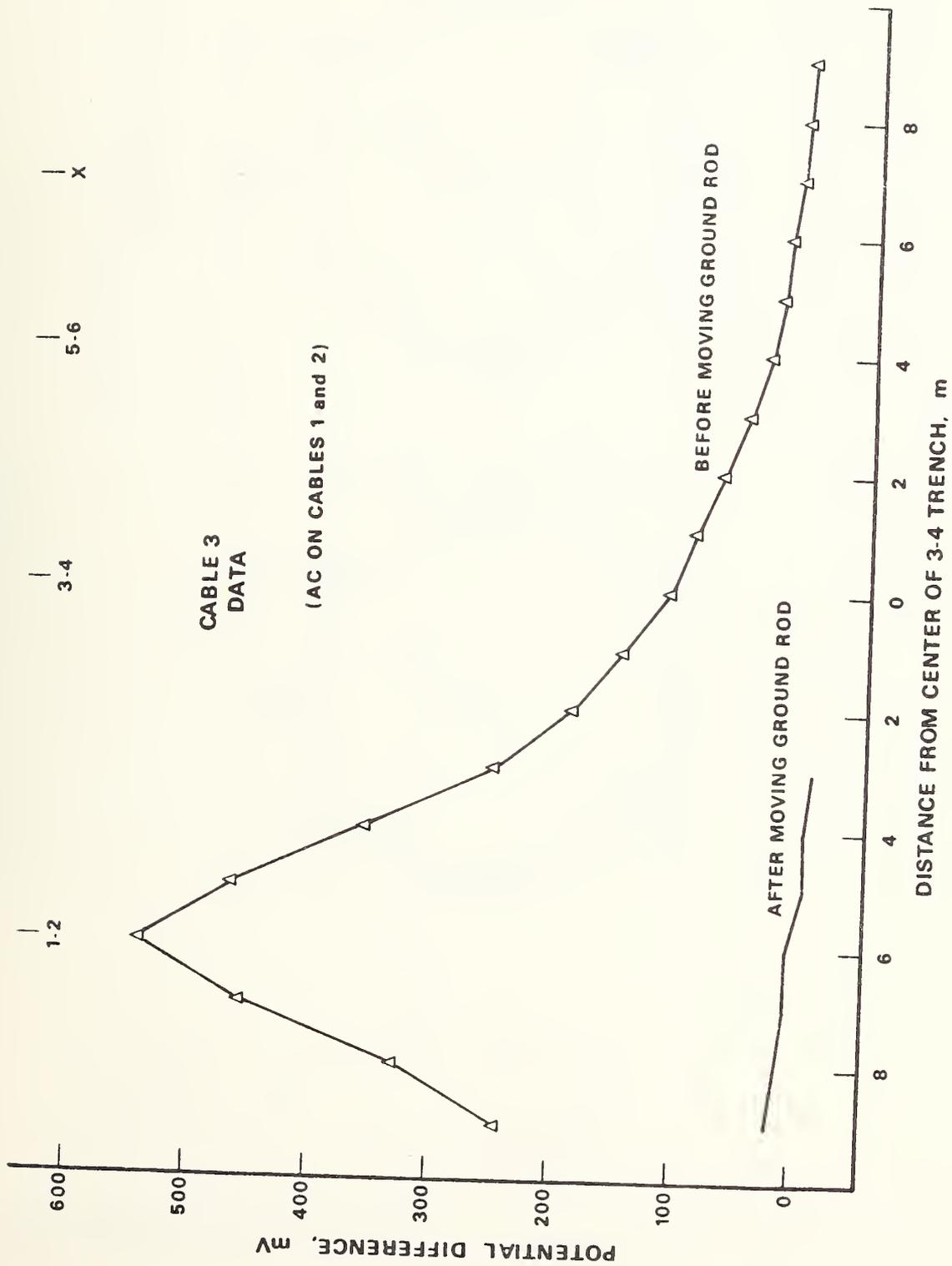


Fig. 19. The results of moving the ground rod and introducing the isolation transformer.

EARTH CURRENT MEASUREMENT
(POTENTIAL BETWEEN TWO Cu-CuSO_4 ELECTRODES)

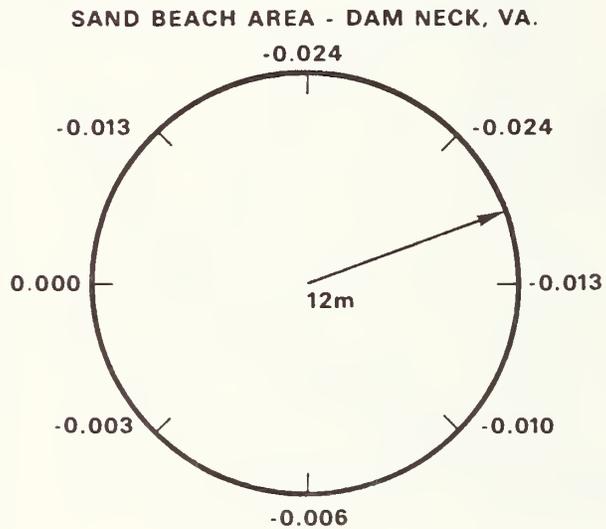
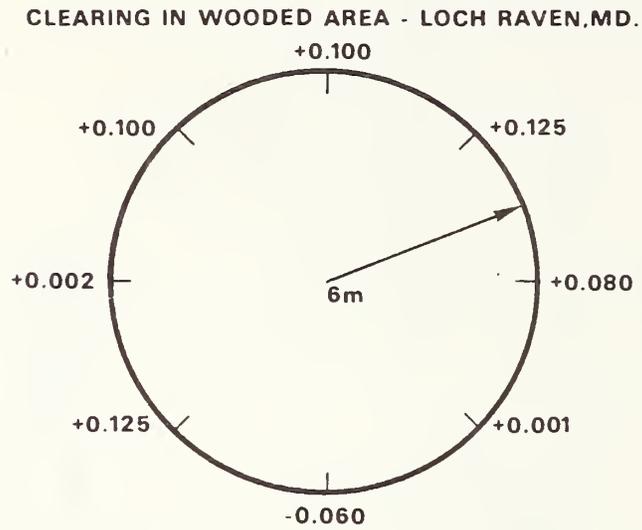
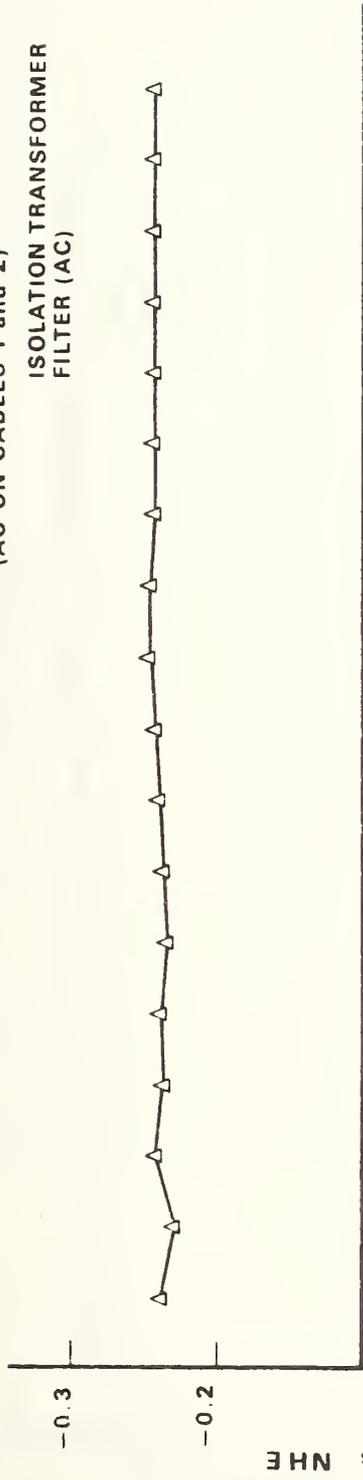


Fig. 20. Earth current measurements at Loch Raven, MD and Dam Neck, VA.

CABLE 3
DATA

(AC ON CABLES 1 and 2)
ISOLATION TRANSFORMER
FILTER (AC)



NO AC

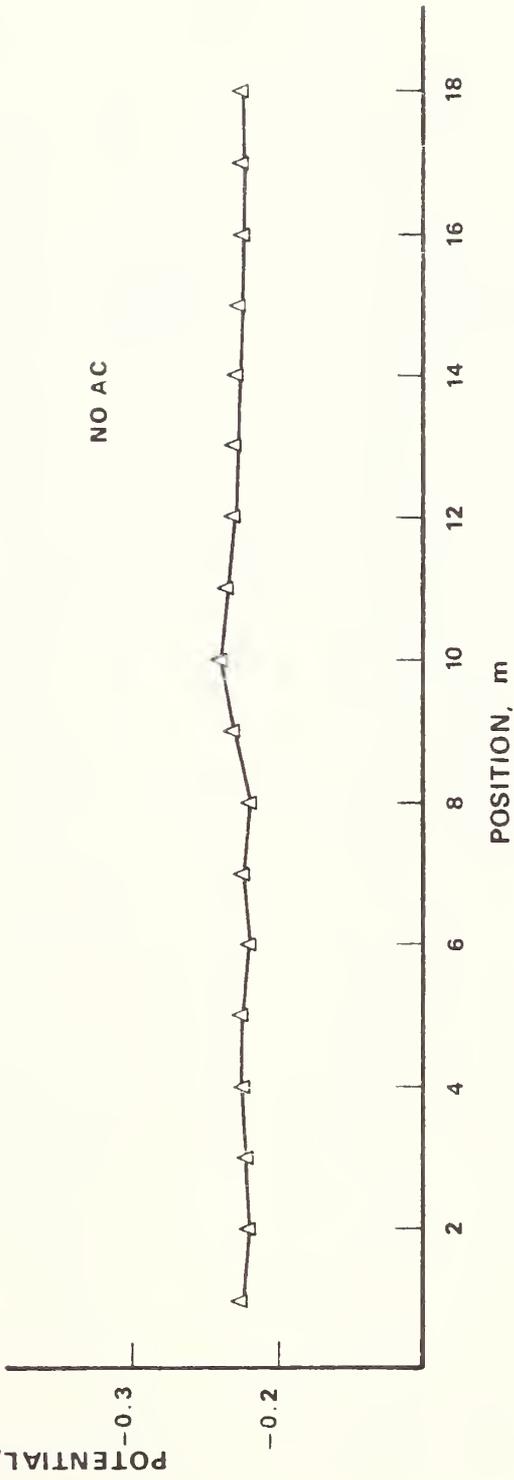


Fig. 21. The effects of stray currents on potential.

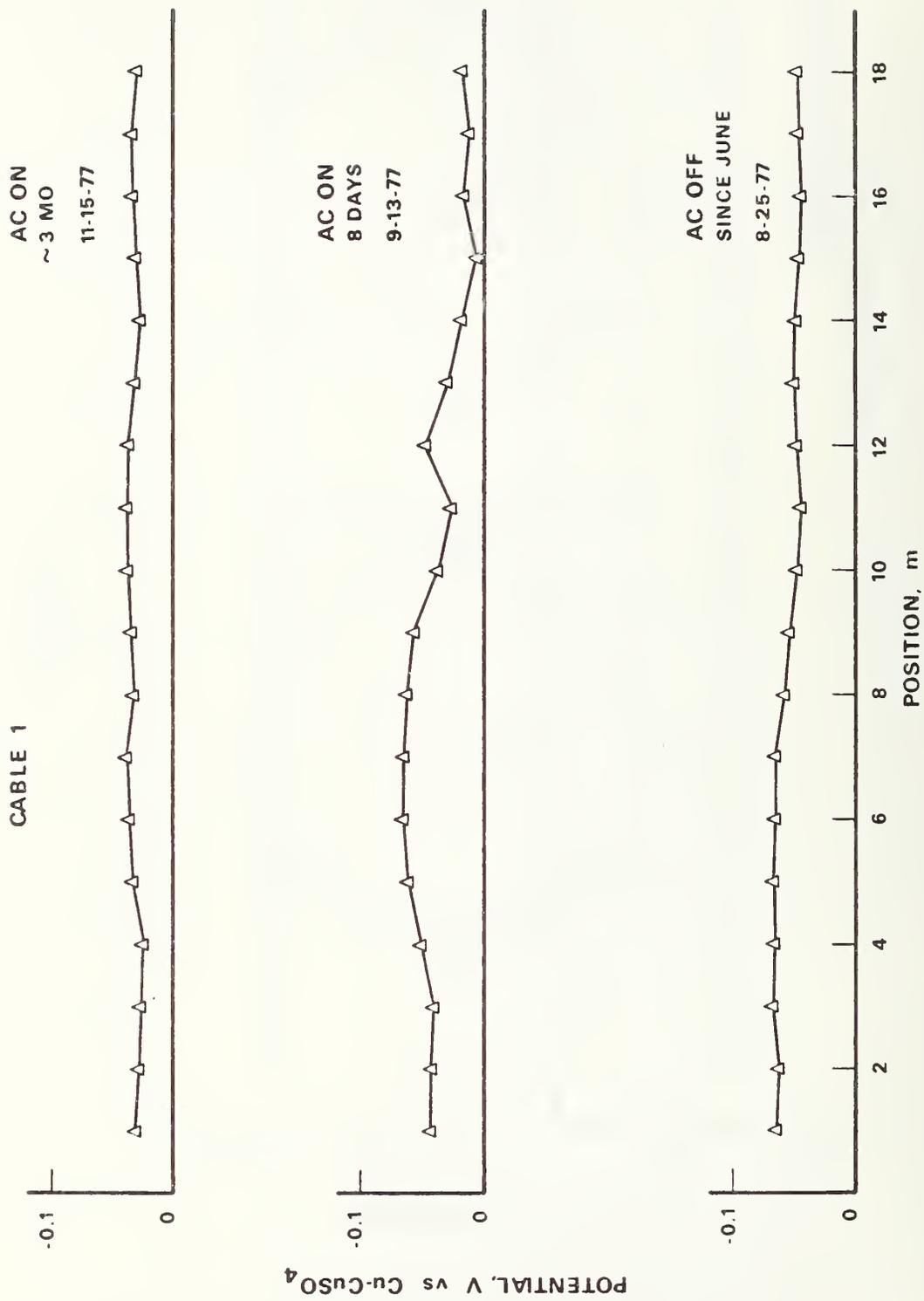


Fig. 22. Stabilization of the ac potential.

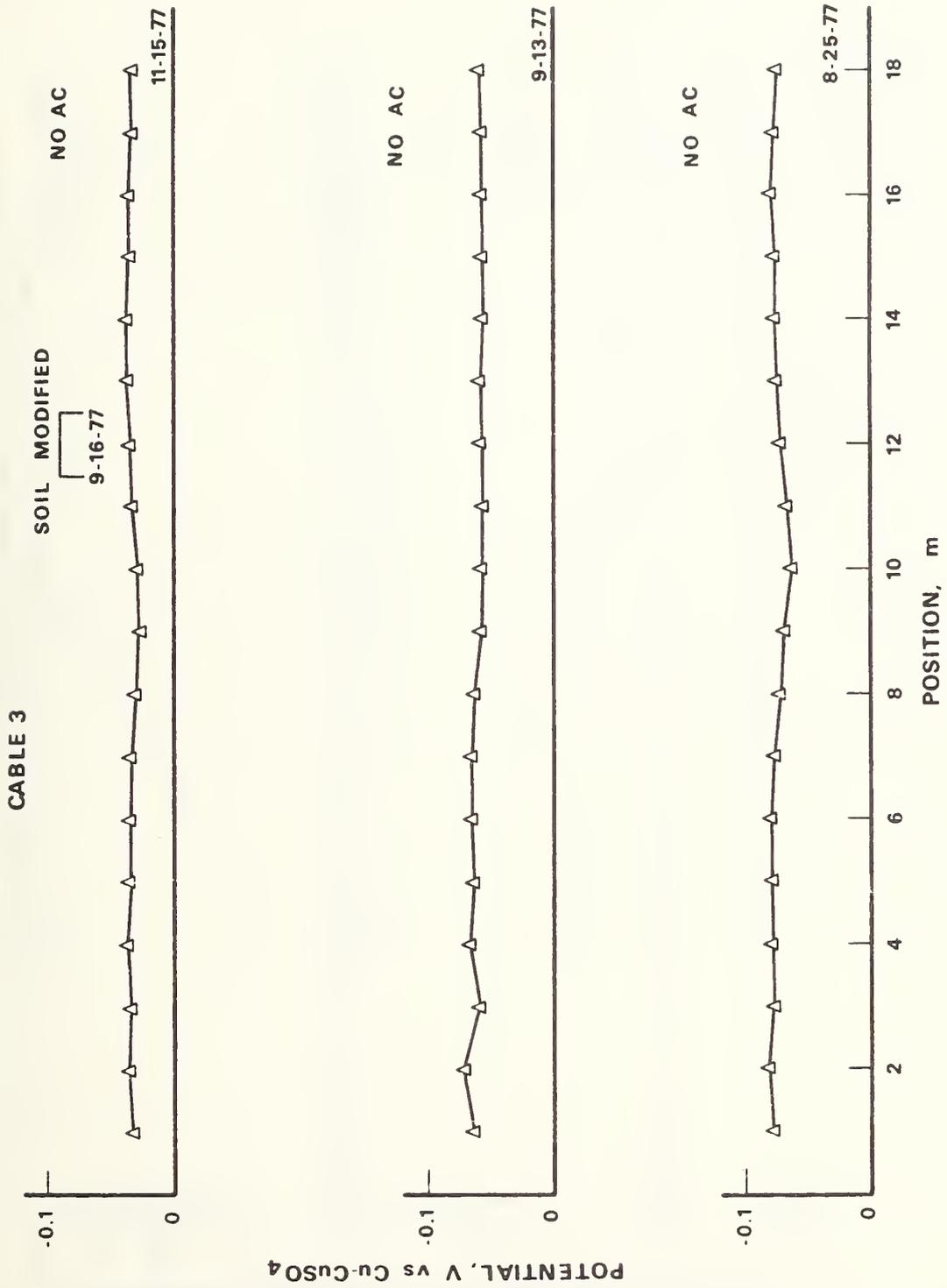


Fig. 23. The effects of modification of soil on potential.

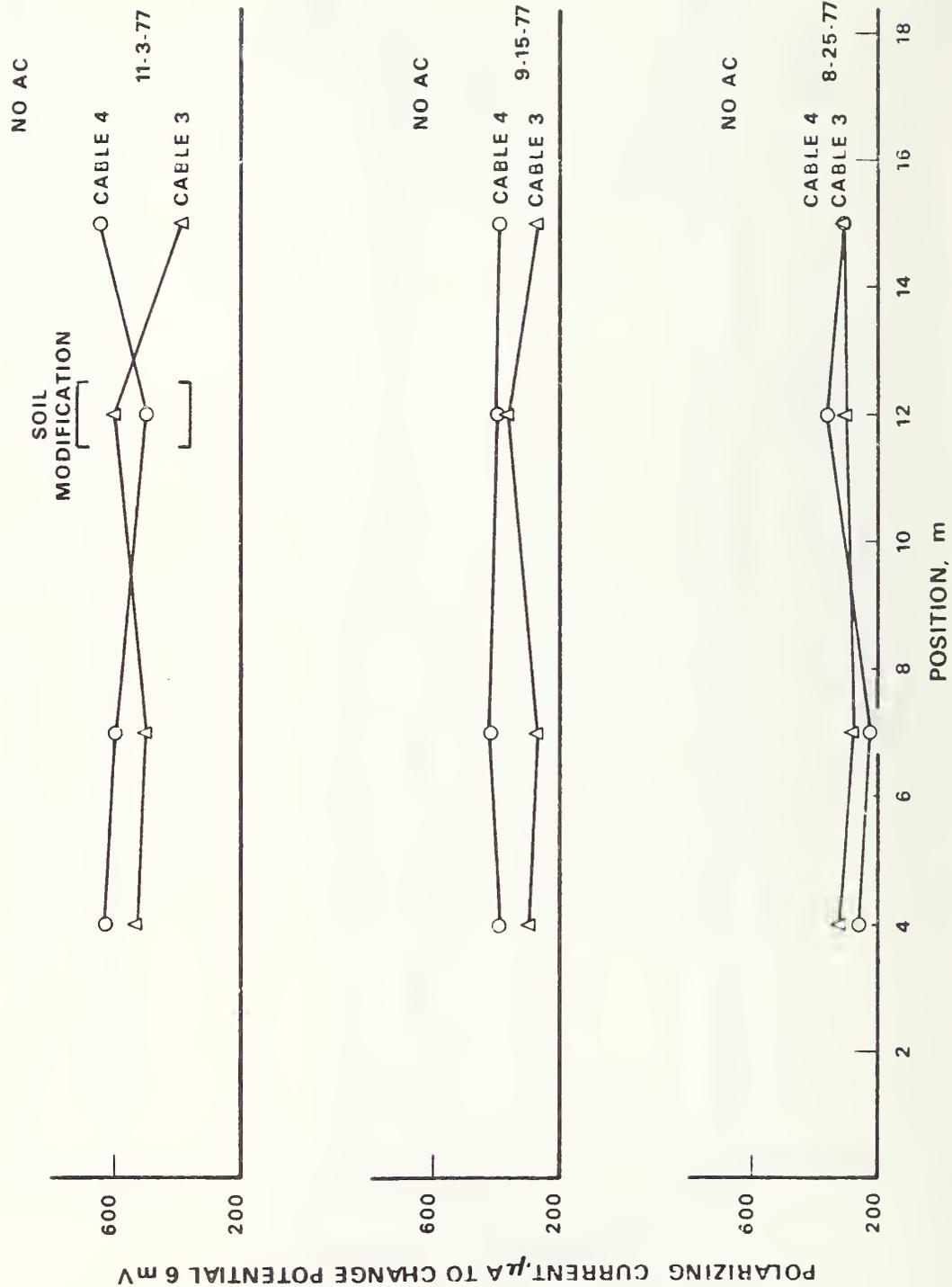


Fig. 24. Polarization of cables 3 and 4 without AC.

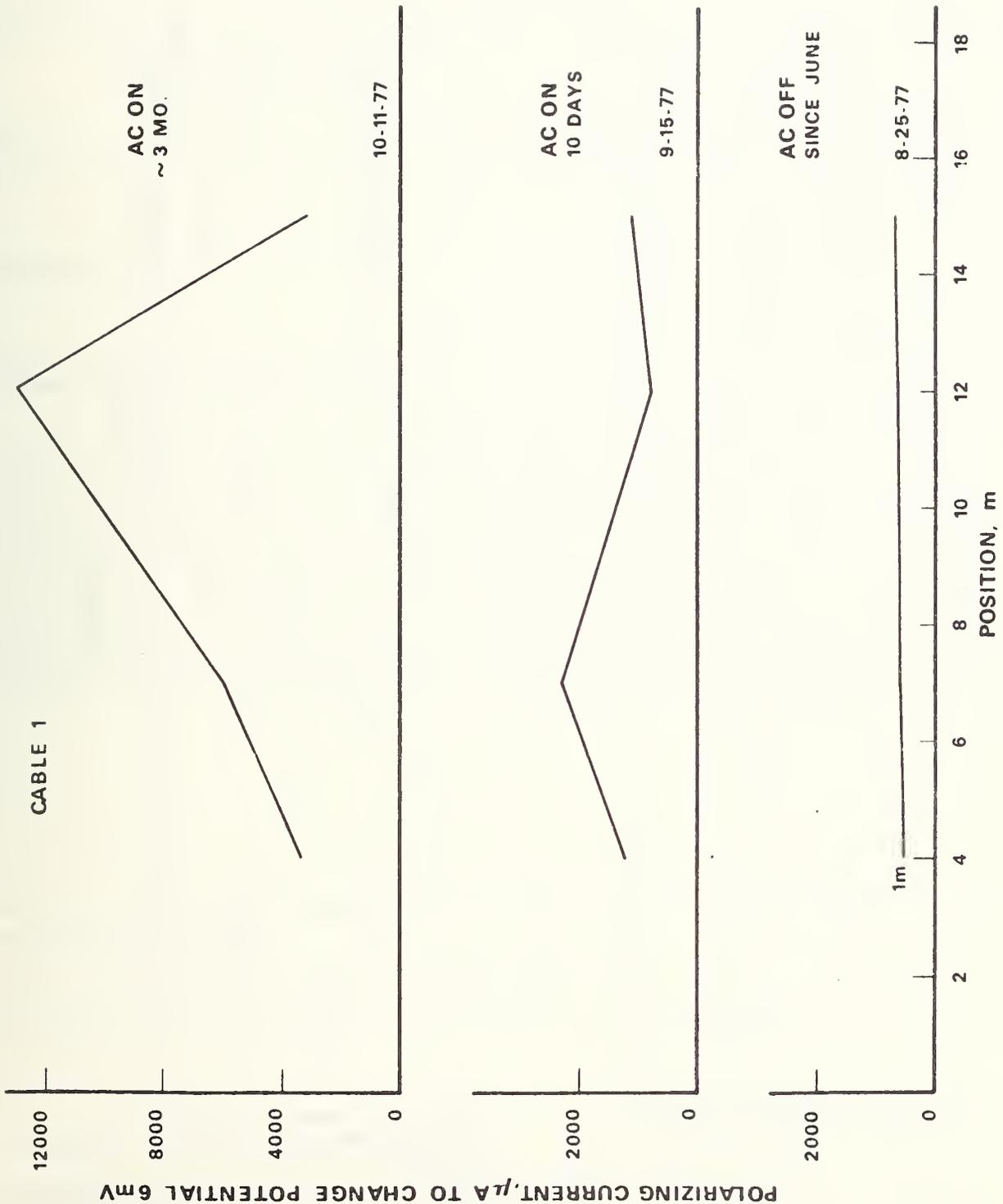


Fig. 25. The current produced by polarizing cable 1 to 6 mV.

CABLE 3

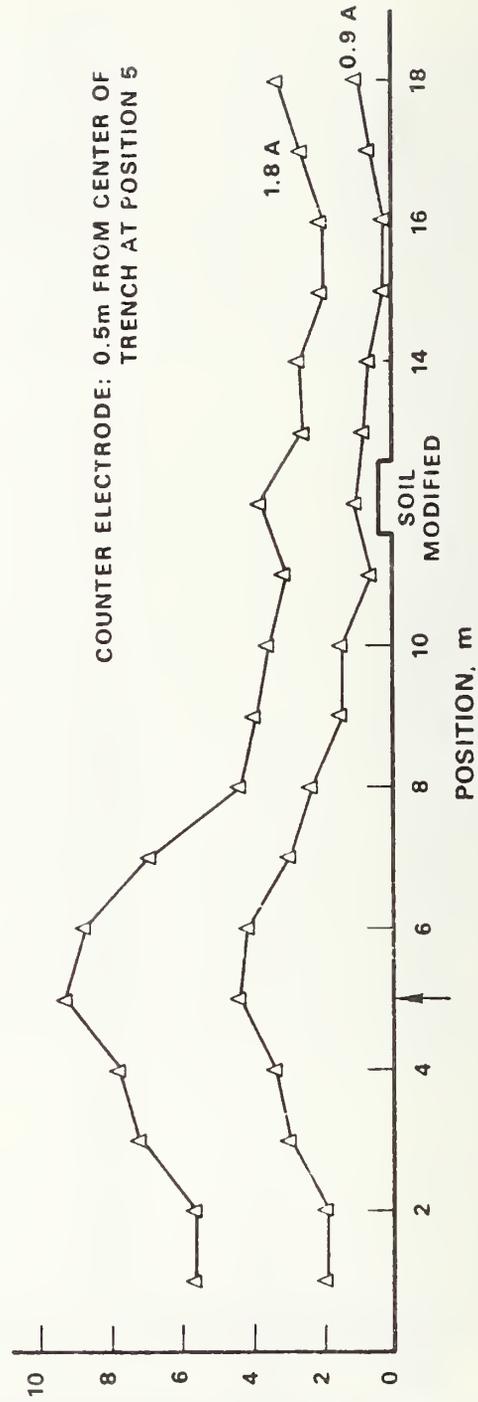
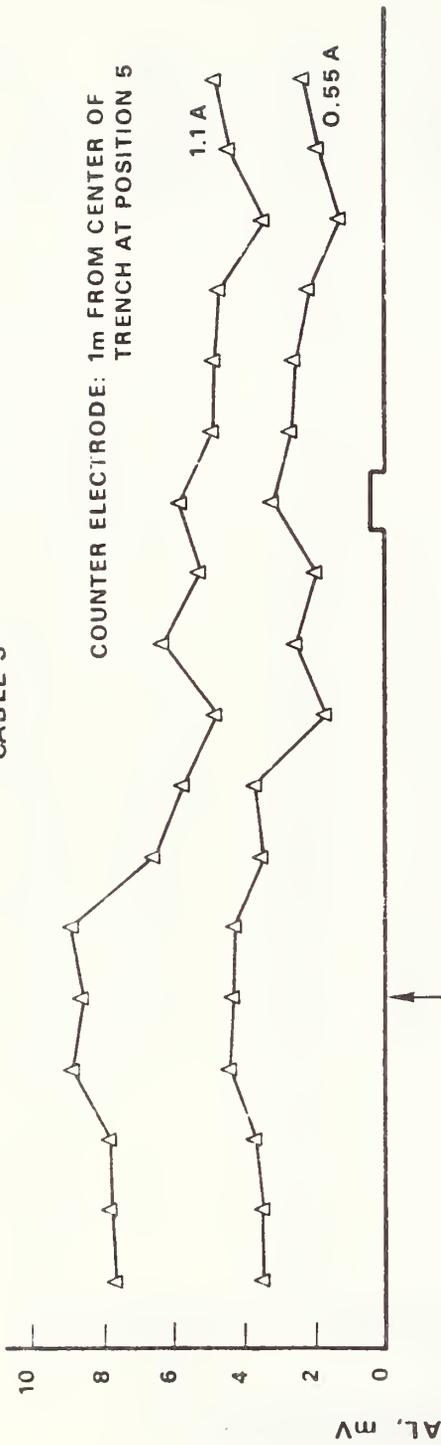


Fig. 26. Distribution of current along cable.

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15. SUPPLEMENTARY NOTES			
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.) <p>The report describes the work done on the second year of a three-year project whose purpose is to develop in-situ methods for detecting corrosion on buried copper concentric neutral (CCN) wires. Potential and polarization measurements on buried cables have been performed, and methods for distinguishing the signals of interest from interference due to a.c. applied to the cables, as well as d.c. earth currents, have been developed. The soil around one of the buried cables has been modified in order to make the environment more corrosive.</p> <p>Laboratory measurements to test possible corrosion detection techniques have been performed. Current-potential data so far obtained have been analyzed. Impedance measurements have also been tested, but results indicate that the method is not very well suited for corrosion detection. Analysis of electrochemical noise has been developed and tested, and measurements on some electrochemical systems carried out.</p>			
17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons) Buried cables; copper concentric neutral wires (CCN); corrosion detection methods; current-potential measurements; underground corrosion			
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